ENVIRONMENTAL CONTROLS AND ECOLOGICAL CONSEQUENCES OF REGIONAL PRECIPITATION CHEMISTRY IN MINNESOTA

A THESIS

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ABSTRACT

Precipitation chemistry in central North America appears to be controlled by interactions of anthropogenic acid aerosols from the urban-industrial region of the Lower Great Lakes and Ohio Valley with alkaline dust and gaseous NH_3 emitted from cultivated prairie soils. Analyses of major ions and trace metals in precipitation events and snow core samples from sites along a 600 km transect from the North Dakota prairie to the northeastern Minnesota forest indicated that loadings and concentrations of Ca^{++}, Mg^{++}, and other soil-derived material decreased with increasing distance from the prairie. Acidity was highest in the east and decreased to the west. Sulfate has both natural sources in the west and anthropogenic sources in the east; its concentration was least at sites in the middle of the transect. Acidity increased and inputs of soil-derived elements decreased during winter when snow and freezing temperatures reduced wind erosion and bacterial decomposition.

Atmospheric inputs of N and P may be beneficial to nutrient-poor ecosystems in the region. However, precipitation in the eastern portions of the region, which are highly sensitive to acid inputs, is approaching levels of acidity known to cause adverse effects. Any increase in acid loading will increase this danger.

INTRODUCTION

The phenomena of acid precipitation and its effects upon aquatic and terrestrial ecosystems have been recognized for decades. Current knowledge about the causes and effects of acid precipitation is reviewed in Dochinger and Seliga (1976), Kramer (1978), Galloway et al. (1978), Likens et al. (1979), Howells (1979), O'Neill (1979), and Hutchinson and Havas (1980). The consensus is that acid precipitation is caused by a mixture of strong acids, primarily H_2SO_4 and HNO_3, resulting from fossil fuel combustion. Toxic trace metals, such as Pb, Zn, and Cd, (Streumpler 1976, Semb 1978) and organic micropollutants, such as polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) (Lunde et al. 1977, Eisenreich et al. 1979) are also associated with acid precipitation. In poorly buffered watersheds acid deposition leads to acidification of lakes and streams and consequently to changes in species composition and abundance at all trophic levels. Terrestrial effects are not well documented, but soil acidification and nutrient leaching (McFee 1978), as well as interferences with the nitrogen cycle (Tamm 1976) have been postulated.

Cogbill and Likens (1974) and others since have noted that the extent and severity of acid precipitation in North America are increasing. Recent data indicate that an area east of the Mississippi River extending north to the Canadian Arctic is subject to acid precipitation ($pH \leq 5.6$) (Whelpdale 1979 Gibson and Baker 1979). This area is partly coincident with the region of most dense SO_x and NO_x emissions (Likens et al. 1979

Husar and Patterson 1980), but other factors must also affect the location and extent of the area subject to acid precipitation.

Alkaline dusts generated by wind erosion and emissions of gaseous NH_3 generated by bacterial action in the cultivated mid-western prairie are two factors potentially affecting the extent of acid precipitation (Winkler 1976). Smith et al. (1970) noted an increase in dust deposition across North America from the humid northeast to the semi-arid central United States. Dust pH also increased from faintly acid to distinctly alkaline along this gradient. Denmead et al. (1974) and Lenhard and Gravenhurst (1980) observed fluxes of NH_3 from the soil to the atmosphere over Australian sheep pastures and rural Western Germany, respectively. Ammonia emissions would likewise be expected from agricultural regions in North America. Lau and Charlson (1977) calculated atmospheric NH_3 concentrations that were highest over the mid-western United States and decreased toward the coasts. Neutralization by soil dusts or gaseous NH_3 would reduce precipitation acidity even where the presence of acid precursors, SO_x and NO_x, might otherwise be expected to cause it.

The gradient in alkaline dust-fall and precipitation pH has been observed on a smaller regional scale in and around Minnesota. Gorham and Tilton (1978) found a decline in the mineral content of Sphagnum fuscum from west to east across Minnesota, which they attributed to a gradient in dust deposition. The pH and concentrations of particles, P_{tot}, Ca^{++}, Mg^{++}, NO_3^-, $SO_4^=$, and SiO_2 were much less in snow from the forested Experimental Lakes Area (ELA)

of northwestern Ontario (Barica and Armstrong 1971) than in snow from the North Dakota prairie (Adomaitis et al. 1967). Gorham and Underwood (Gorham 1976) observed a decrease in pH, specific conductivity, filterable solids, and P_{tot} in snow samples collected along a transect from the North Dakota prairie to eastern Minnesota forests after a blizzard in 1975; pH decreased from 8.0 to 4.9 and conductivity, solids and P_{tot} decreased by 45, 94, and 77%, respectively. Elevated concentrations of PCBs in Lake Superior surface sediments, even where local sources are minimal, indicate long-range transport of anthropogenic material to Minnesota from the Lower Great Lakes-Ohio Valley region (Eisenreich et al. 1979). Calculations of airmass trajectories and observations from satellites confirm that long-range transport of pollutants from that region affects Minnesota (Lyons et al. 1978). The balance between influxes of alkaline material from the west and acid material from the east should therefore control precipitation chemistry in Minnesota. In order to investigate the effect upon precipitation of the interaction between acid and alkaline materials I carried out a study -- in cooperation with J. David Thornton -- of precipitation chemistry at three sites across northern Minnesota and eastern North Dakota. This study also provides baseline data necessary to assess the impact on precipitation of increased acid inputs or changes in the influx of alkaline dust. Development of additional coal-fired power plants and a proposed copper-nickel smelter in the region, and continued increase in NO_x and SO_x emissions throughout North America, would increase acid inputs.

Alkaline inputs would be expected to increase if the cultivation of prairie soil were intensified or expanded to include presently uncultivated land, but improved soil conservation practices could lessen erosion and decrease the influx of soil dusts.

METHODS

Sample Collection

Precipitation samples were collected at three sites along a transect from the prairie of eastern North Dakota to the northeastern Minnesota forests (Fig. 1). The western site, at the Tewaukon Wildlife Refuge, is surrounded by a 1-2 km buffer of grassland, marsh, and lakes within an intensively cultivated region, and was chosen to provide precipitation dominated by the alkaline influence of dust and ammonia. The Hovland site, located in a remote forested area of northeastern Minnesota far from appreciable local pollutant or dust sources, was chosen to provide precipitation influenced primarily by long-range transport of acid anthropogenic material. The Itasca site, midway between the other two sites and 50 km east of the forest-prairie transition, was chosen to provide precipitation influenced by a mixture of acid and alkaline inputs. To supplement the precipitation data, snowpack samples were taken at the collector sites and at intermediate locations (as indicated in Fig. 1). The collector and snow-coring sites are described in more detail in Appendix 1.

I used Aerochem Metrics automatic wet-dry precipitation collectors to sample wet-only precipitation and dry fallout. This sampler was also chosen for use in the network of the National Atmospheric Deposition Program. Wet precipitation was sampled on an event basis; dry fallout was collected over longer intervals. This sampling scheme retained maximum information about variations among individual storms and minimized contamination and alteration of samples in the field (Galloway and Likens 1978). Appendix 2 describes the collectors used in the study and the acid-washing procedure used to clean the collection buckets.

I sampled the snowpack by inserting a 38.5 cm^2 plexiglass tube vertically into an undisturbed area of the snowpack and digging a pit next to it to enable removal of the intact core (cf Wright and Dovland 1978). The snow in the tube was put into a polyethylene bag, sealed, brought back to the laboratory and stored in a freezer until analyzed. Multiple cores were bagged together if the snow was shallow. I also sampled individual layers within the snowpack by inserting the coring tube horizontally.

To prevent contamination of the snowpack by material at the ground surface and, as far as possible, loss of meltwater by seepage I placed polyethylene sheets on the ground at the three collector sites and at two additional sites in northeastern Minnesota (sites 30 and 32 in Fig. 1) before the winter of 1978-79. At these five sites vertical cores were taken over the plastic sheet.

Sample Analysis

Personnel at the sites sealed the wet-collection bucket after each event and shipped the sample by parcel post to the laboratory located at the University of Minnesota. If the volume was less than about 200 ml the sample was sent in an acid-cleaned polyethylene bottle and the bucket was reused. When the sample arrived (usually within 4 days) I measured its pH and conductivity. If it was not a small sample shipped in a bottle, an aliquot was removed and acidified to 1% with HNO_3 and used for trace metal determinations -- performed by J. David Thornton -- using flameless AAS. Analytical procedures for trace metals followed the manufacturer's recommendations (Perkin Elmer) and are described in detail by Thornton (1981).
I removed 25 ml of sample and froze it in a flask for later determination of total phosphorus (P_{tot}) by a molybdate-blue method (Eisenreich et al. 1975). If the pH of the sample was greater than 5.5 and there was sufficient volume, alkalinity was measured by the Gran Titration method (Dryssen and Sillén, 1967, Stumm and Morgan 1970). An aliquot was also filtered through a 0.4 μm polycarbonate filter (Nuclepore). Half the filtrate was stored in the dark at 4° C and the other half was frozen. The filter residue was dried at 105°C and weighed. The unfrozen aliquot was used for determination of Na^+, K^+, Ca^{++}, and Mg^{++} by Atomic Absorption Spectrophotometry (AAS); the frozen aliquot was used for Cl^-, NO_3^-, and $SO_4^=$ determination by Ion Chromatography (IC). The remainder of the sample was put in a fresh, acid-cleaned bottle and stored in a refrigerator; a portion of this was used

for NH_4^+ determination by the phenolhypchlorite method (Solórzano 1967, Stainton et al. 1977). Because of analytical problems NH_4^+ was not analyzed until after a long storage period, but analyses of standard solutions stored with the samples suggested that sample alteration was minimal in most cases. Appendix 3 gives a more detailed description of the analytical procedures used.

Analytical Quality Control

For major ions the estimated analytical accuracy -- expressed as percent relative error -- was within 1% and the precision -- expressed as coefficient of variation -- was within 4%. Blank determinations were generally negligible. Measured concentrations in simulated precipitation standards gave excellent ionic balances over a 20-fold concentration range from 75 to 1500 $\mu eq\ l^{-1}$, and the response to dilution was linear. Appendix 4 presents the precision and accuracy estimates, analytical results for simulated precipitation standards and blanks, and estimates of detection limits.

I checked the sums of major cations and anions for all samples that were analyzed completely. The ionic balances for volume-weighted mean concentrations, expressed as anion/cation ratios were as follows: Tewaukon 1.04, Itasca 0.98, Hovland 0.99, 1978 snows 0.96, 1978-79 snows 0.94. The balances in individual samples, however, often deviated significantly from 1.00 (see Appendix V). Anion/cation balances in precipitation samples (Scheider et al. 1979, NADP 1978, 1979), and extremely dilute lakewater samples from

Minnesota and Wisconsin that were analyzed by the USGS laboratory (Gorham et al. in prep.) also deviate significantly from 1.00. The relatively large errors associated with measuring concentrations near the analytical detection limits may be responsible for much of the deviation from perfect ionic balances. Interactions with particulates and/or the presence of non-ionic forms of some elements may also contribute to this problem.

The anion/cation ratios and absolute difference between anions and cations, after adjusting the Cl^- concentrations to more realistic values based on Junge's (Junge and Werby 1958) and the NADP (NADP 1978) network's data, suggest that fine particulates associated with soil dust are partly responsible for the poor ionic balances. When values of 2.8, 4.2, and 5.6 $\mu eq\ \ell^{-1}$ are substituted for the Cl^- concentrations at Hovland, Itasca and Tewaukon, respectively, cations exceed anions by 36, 49 and 55 $\mu eq\ \ell^{-1}$ (yielding ratios of 0.64, 0.56, and 0.61). The greatest excess of cations occurred at Tewaukon where the influence of soil dust (and presumably fine particulates) upon precipitation is greatest. Some cations associated with fine particulates could be released in the flame used in Atomic Absorption Spectrophotometry, but Ion Chromatography would only detect the ionic forms of $SO_4^=$, NO_3^-, and Cl^-.

The volume-weighted mean concentrations -- expressed as equivalent percentages -- in samples with anion/cation balances between 0.90 and 1.10 did not differ systematically from the

concentrations in all samples (see Fig. 2). The observed differences are slight and generally no more than would be expected when comparing a small subset to the full data set. However, the most acid samples appear to be overrepresented in the well balanced group. The ionic balances are discussed further in Appendix 5.

RESULTS

Concentrations in Event-Samples

During the 14-month study period 47, 79, and 81 samples of individual precipitation events were collected at Tewaukon, Itasca, and Hovland, respectively. The analytical results for these samples are presented in Appendix 6. Tables 1 and 2 present the ranges and volume-weighted and geometric means. For each parameter the ranking and significant differences among the sites are indicated. For the major ions and P_{tot}, common superscripts indicate that the means are equivalent at those sites. Significant differences among the geometric mean trace-metal concentrations are indicated by asterisks. Volume-weighted mean concentrations for trace metals that were undetectable in some samples were estimated with the average of 0.0 and the detection limit substituted for samples in which the metal was undetectable (see Thornton 1981).

The volume-weighted mean concentration of H^+ increased 4-fold from west to east . Metal cations, Ca^{++}, Mg^{++}, Na^+, and K^+, decreased 2 to 2.5-fold from west to east. The concentrations of NH_4^+ and the acid anions, NO_3^- and $SO_4^=$, tended to be lowest

at Itasca and higher at the other sites, though NO_3^- varied the least. Although there was a suggestion of a decrease from west to east, Cl^- concentrations were unrealistically high due to analytical problems and/or contamination.

Chloride concentrations and Cl^-/Na^+ ratios were distinctly lower in precipitation samples from this region collected by Junge (Junge and Werby 1958) or by the NADP network (Gibson and Baker 1979). I do not believe that residual HCl from the bucket-washing was involved because there was no systematic relationship between pH and Cl^- concentration in the samples. Inadvertent handling of the bucket interior by field personnel or contamination by caps on the bottles used to store the samples prior to ion determinations, are potential sources of Cl^- contamination.

Mean concentrations of P_{tot} declined from Tewaukon to Itasca, but because of a small number of samples at Hovland that contained pollen, seeds, or other organic debris, the volume-weighted mean concentration of P_{tot} was nearly as high there as at Tewaukon. However, the geometric mean concentration at Hovland was lower than at either Tewaukon or Itasca, as would be expected if soil was the primary source of P. Both particulates and alkalinity (the latter now shown in Tables 1 and 2) decreased from Tewaukon to Hovland, however, they were not determined in all samples. Most trace-metal concentrations (Thornton 1981) decreased from Tewaukon to Hovland; Al, Fe, and Mn, which decreased most steeply, were 4- to 6-fold less at Hovland than at Tewaukon. The lowest Pb and Cu concentrations, however, were observed at Itasca. The trace metal data are discussed further by Thornton (1981). The frequency distributions of major ion

and P_{tot} concentrations, which are presented in Appendix 7, illustrate further the concentration trends among the sites.

Specific conductivity was highest at Hovland because of the high H^+ concentration; the lowest conductivity was observed at Itasca. The conductivity due to ions other than H^+ was less at Hovland and Itasca than at Tewaukon.

Table 3 shows that the importance of H^+ increased from Tewaukon, where it was least important, to Hovland, where concentrations of H^+ and Ca^{++} were exceeded only by NH_4^+. The importance of Ca^{++}, relative to H^+ and NH_4^+ was least at Hovland. Ammonium, which is present both as a gas and as a fine aerosol would be expected to travel farther from the western prairie than Ca^{++}, which is present predominantly in coarse particulates (NRC 1978). The remainder of the cations had the same relative order at all three sites. The concentration of $SO_4^=$ exceeded NO_3^- at all three sites, and only at Tewaukon was HCO_3^- more than a minor constituent of precipitation. As noted previously, Cl^- was probably unrealistically high.

Wet Deposition

Monthly mean concentrations, weighted by volume, were calculated from all samples available during a month and multiplied by the total precipitation volume for the month to get an estimate of wet deposition on a monthly basis. I summed

the monthly estimates of wet depositions over three overlapping 12-month periods (May-April, June-May, July-June), within the 14 months of sample collection and used the average of the three sums as an estimate of wet deposition (Table 4).

Precipitation at Hovland was 1.7-fold greater than at Tewaukon. Wet deposition of H^+, $SO_4^=$, NO_3^-, and NH_4^+ increased by factors of 7.8, 2.1, 1.4, and from Tewaukon to Hovland. Potassium deposition followed an inverse trend; it was greatest at Tewaukon and least at Hovland, but varied only slightly. Because of the substantially greater precipitation volume (1.7) at Itasca, deposition of the remaining cations, Ca^{++}, Mg^{++}, and Na^+, was greater at Itasca that at Tewaukon, even though the concentrations were higher at Tewaukon. Wet deposition of these metal cations was least at Hovland. Phosphorus deposition was least at Itasca. Annual deposition of P_{tot} at Hovland was higher than at Tewaukon because of P enrichment during the spring when pollination and seed dispersal occurred. In most ecosystems such plant-derived P is internally cycled P, not a new input to the system. However, for lakes, and perhaps for some terrestrial sites where pollen production is slight, this P may be a new input. input.

Dry Fallout

Collection of uncontaminated dry fallout proved to be exceptionally troublesome. Bird feces rendered most of the dry-fall samples unusable. In 250 ml suspensions of dry fallout,

NH_4^+ and P_{tot} were well above the concentration in the highest standards; 2 mg ℓ^{-1} for NH_4^+-N and 200 µg ℓ^{-1} for P_{tot} (8 mg m^{-2} and 800 µg m^{-2}). During the spring of 1979 I installed a device to discourage birds from perching on the rim of the dry-collector bucket (cf Egnér et al. 1949). This ring of prongs is pictured in Fig. 1 of Appendix 2. The bird-off was partially successful, but I had to suspend sample collection before many dry-fall samples free of feces could be collected. In addition some very light snowfalls were collected in the dry bucket because there was insufficient moisture to activate the sensor. The samplers operated as bulk collectors during part of the winter because of power supply and sensor malfunctions.

In spite of the sampling difficulties, I collected a small number of relatively clean dry-fallout samples from each site. Data for these samples are given in Appendix 8. Dry-deposition estimates, from samples collected concurrently at the three sites during spring of 1979, are given in Table 5a. The alkalinity of the dust, as indicated by the pH of a 250-ml solution, increased from Hovland to Tewaukon. Dry deposition of Ca^{++}, Na^+, K^+, NO_3^-, $SO_4^=$, and P_{tot} was highest at Tewaukon. Deposition of Mg^{++} was greatest at Itasca. Dry deposition of both SO_4^+, and NO_3^-, which have anthropogenic sources, was greater at Hovland than at Itasca. Dry deposition of Ca^{++} and Mg^{++} was lowest at Hovland.

Table 5b presents the estimated annual dry deposition calculated from all available measurements at the three sites. Some samples that were only slightly contaminated or that could be cleaned before the dust was dissolved are included in these estimates, so the actual

dry-fall input of some elements may be somewhat less than estimated. Annual estimates indicate trends similar to those indicated by the spring data; pH and deposition of P_{tot}, Ca^{++}, NH_4^+, and total solids decreased from Tewaukon to Hovland. Nitrate and $SO_4^=$ deposition were lowest at Itasca. The reliability of these data is unknown because of possible contamination, and the small number of samples, which may not be representative of the entire year. However, the observed trends for particulates, pH, P_{tot}, and Ca^{++} fit the patterns expected from previous knowledge about dustfall gradients across Minnesota. Dry deposition of NO_3^-, and $SO_4^=$ was least at Itasca; this same trend was observed in wet precipitation and snow-core concentrations. The estimates of dry deposition are less than the wet deposition estimates for all ions except K^+ and P_{tot}, which had approximately equal wet and dry depositions. These results for dry deposition should be interpreted cautiously; an open bucket will not have the same collection efficiency for gases, aerosols, and particulates as natural vegetation, soil, or water surfaces, and may under or overestimate inputs of some materials.

Seasonal Trends

In order to identify seasonal trends that were obscured by short-term fluctuations in the monthly, volume-weighted mean concentrations and monthly depositions (see Appendix 9), I calculated mean concentrations and depositions on a seasonal basis. The seasons, referred to as spring, summer, fall, and winter, begin with April 1978 and are each 3 months long. The seasonal mean concentrations are presented in Table 6. The ions are listed in the

table according to their ranking in volume-weighted mean annual precipitation; the numbers in parentheses indicate the ion ranking for each season. Presenting the data in this way illustrates the shifts in ion dominance that occur over the year.

The concentration and importance of H^+ was greatest at all sites during the winter when snow blanketed the soil and freezing temperatures reduced microbial generation of NH_3. Winter concentrations of H^+ were approximately double the annual means. Even individual snow events at Tewaukon, which is surrounded by cultivated fields, were acid (pH < 5.0). The H^+ increase was accompanied by a decrease in concentration and importance of Ca^{++}, Mg^{++}, NH_4^+, amd K^+. At Hovland, where winter H^+ concentration increased the most over other seasons, the concentration and importance of $SO_4^=$ and NO_3^- were also greatest during the winter. This is especially noteworthy because the scavenging efficiency of snow is probably less than that of rain (Gorham 1976, Scott, 1978). High $SO_4^=$ and NO_3^- concentrations in winter may indicate changes in weather patterns affecting long-range transport of these acid materials. Slower reaction rates for their formation from gaseous precursors during the drier, colder, less sunny winter would allow for longer transport before their removal from the atmosphere. Different sources of acid precursors or the lower mixing height during winter may also affect the inputs of $SO_4^=$ and NO_3^-.

The concentration of P_{tot} was highest at Tewaukon and Itasca during the fall when the prairie was dry and crops were being harvested. At Hovland, however, maximum P_{tot} concentrations occurred during the spring, and as noted previously, appeared to

correspond to pollination and seed dispersal by the surrounding vegetation; P_{tot} concentrations during the fall at Hovland were slightly elevated relative to summer and winter. From the seasonal values it is evident that it was the elevated P_{tot} at Hovland in the spring that gave a high annual mean P_{tot} concentration. During the remainder of the year P_{tot} concentrations were much less at Hovland than at Itasca or Tewaukon.

Except when unusually large volumes of precipitation offset low concentrations (as occurred at Itasca during the summer) the seasonal trends in wet deposition followed the concentration trends (see Table 7). Approximately half the total annual wet deposition of H^+ at Tewaukon and Hovland came during the period from January through March. Even more H^+ would be stored in the snowpack, which accumulated from November to early April; this mass of H^+ was released over a short period in the spring.

Concentrations in Snowpack Samples

The analytical results for the snowpack samples are presented in Appendix 10. Table 8 presents the ranges and means of pH, conductivity, and concentrations of major ions, P_{tot}, and particulates. in 42 samples collected during mid-March 1978 in northeastern Minnesota. Means, standard errors, and number of samples (N) are also given for samples of fresh surface snow, intermediate horizons, old bottom horizons, and a brown icy crust within the snowpack. Significant differences among the horizons are

noted by asterisks. The snow samples were distinctly acid (pH ≤ 5.0), and H^+ was the dominant cation in the vertical cores and all but the bottom horizons. Calcium was the dominant cation in the bottom horizons. This suggests that snow falling in early winter had higher Ca^{++} concentrations or that dry deposition of Ca^{++} was greater then. Concentrations of airborne dust available for incorporation into the snowpack would be greatest in late fall and early winter, before much of the prairie was covered with snow. The concentrations of NO_3^- and $SO_4^=$, the dominant anions, were nearly equal in the vertical cores. However, in the intermediate horizons NO_3^- was 1.6 times $SO_4^=$.

Conductivity and concentrations of most ions were highest in the intermediate horizons. The higher concentrations may be due to dry deposition augmenting the snowfall inputs or to sublimation of water when that layer was topmost. The low concentrations in the fresh horizons indicate that the recent snow was relatively clean. Particulates, Ca^{++}, Mg^{++}, and P_{tot} were most concentrated in the bottom horizon, but the other ions were not similarly high in that horizon. Partial melting and flushing of soluble ions, but not ions that are mostly associated with particulates, may occur throughout the winter and be responsible for this.

The icy, brown crusts within the snowpack contained the highest concentrations of Mg^{++} and $SO_4^=$. Magnesium may be associated with dusts transported from distant sources. A

sleet event the following year in late winter at Hovland and Itasca (12 April 1979) that contained red-brown dust also had high concentrations of Mg^{++}. A low-pressure system causing strong upper level air flow from the south-central United States to Minnesota was associated with this storm. Lyons et al. (1978) observed a similar weather system during 1977 that transported soil dust from the south-central United States to Minnesota. It is probable that such a weather system was also responsible for the brown crusts in the 1978 snowpack, as the crusts were formed during mid-winter when local sources of dust would be minimal.

Table 9 presents a regional picture of the ranges and means for conductivity and concentrations of major ions, P_{tot}, and particulates in 43 snow-core samples collected during the winter of 1978-79. The regions roughly correspond to the three event-collector sites. Sites 10, 11, and 12 were grouped as prairie sites, sites 20-25 were grouped as transitional forest sites, and the remainder grouped as northeastern forest sites (see Figure 1). The full data set for these samples is given in Appendix 10.

Specific conductivity and the concentrations of particulates, P_{tot}, alkalinity, Cl^-, NH_4^+, and metal cations decreased from west to east. Ammonium decreased only slightly; the other parameters decreased from 10 to 20-fold. Acidity followed a reverse trend; H^+ increased 100-fold from west to east.

Concentrations of $SO_4^=$, and to a lesser extend, NO_3^- were higher in both the prairie site and northeastern forest site samples than in the transition forest site samples. This suggests that these ions are derived from soil dusts as well as from anthropogenic emissions. Figures 3 and 4 show that the trends in SO_4, pH, particulates and P_{tot}, as indicated by concentrations in samples taken concurrently along a belt transect, are quite similar to those suggested by mean concentrations in all samples taken in the three regions throughout the winter. Sulfate increases to the west of the forest-prairie transition, and also slightly at the most eastern sites. Site 35, which has a higher $SO_4^=$ concentration and lower pH in March than the other northeastern forest sites do is probably influenced by the Duluth-Superior urban area. The January sample from site 23, which was collected over the ice on a back water of the Bigfork River has an anomalously high pH. Similar high pH values were observed in samples collected on the ice at Lake Itasca (not shown in the figure). Both particulates and P_{tot} decreased to the east of the forest-prairie transition.

In samples from the prairie sites Ca^{++} and Na^+ were the most abundant cations and $SO_4^=$ was the strongly dominant anion. Magnesium rather than Na^+ was the important cation with Ca^{++} at the transition forest sites; HCO_3^- and NO_3^- were the dominant anions there. At the northeastern forest sites H^+ was the dominant cation, and NO_3^- followed by $SO_4^=$ were the dominant anions. Alkalinity was negligible in the northeastern forest site samples, but it was present in all the prairie site and many of the

transition forest site samples. Alkalinity was not determined in all of the samples, and it may have been higher than indicated for the prairie sites; HCO_3 appeared to be replenished during some of the titrations (perhaps by dissolution of particles) and accurate measurements were not obtained for those samples.

The pH values in samples of individual snowfalls collected at Tewaukon from mid-January to mid-March were less than 5.0, but the pH in snow cores at the prairie sites over the winter was near 7.0. It appears that the acid in snow was neutralized after it fell by alkaline particles suspended from bare, wind-swept fields and incorporated into the snowpack as snow was blown and redeposited in drifts. The snow samples most heavily particulate-laden had the highest pH values. Sulfate also increased in the prairie snow after it fell; $SO_4^=$ was nearly equal to NO_3^- in event-precipitation at Tewaukon, but it was much greater than NO_3^- in many of the snowpack samples, especially those with high particulate concentrations. Because the windblown dust is primarily coarse particles it would not be transported far from the cultivated prairie and so would not have a major effect on snow in the forested areas (cf. Figs. 3 and 4).

At the northeastern forest sites NO_3^- increased relative to $SO_4^=$ after the snow was deposited. The mean concentration of $SO_4^=$ in snow events at Hovland was much greater than NO_3^-, but in snow there and at other northeastern forest sites these two anions were more nearly equal, or NO_3^- was in slight excess. Nitrate was also greater than $SO_4^=$ in the intermediate horizons of the 1978 snowpack from northeastern Minnesota.

Correlations

Logarithmic correlation coefficients among the soil-derived elements Ca^{++}, Mg^{++}, Na^{+}, K^{+}, Fe, Mn, Al, and P_{tot}, which decreased in concentration from west to east, were generally (but not uniformly) large and significant (see Tables 10, 11, and 12). The trace metals Fe, Mn, and Al, which have only minor sources apart from the soil (Lantzy and Mackenzie 1979), were highly correlated with one another at all three sites, but they were not consistently correlated with the other major cations derived from soils. The lack of uniformly large correlation coefficients among this group of elements and differences among the sites indicates that sources other than soil dust contribute to the inputs of these elements, or that local soil mineralogy varies among the sites. Differences in the abundance of calcium and magnesium carbonates relative to siliceous minerals may well be involved. Sulfate and NO_3^-, which have anthropogenic sources, were highly correlated at the three sites, but the magnitude of the coefficients decreased from east to west. The decrease suggests that one or both of these ions has an additional source in the west, such as soil dust. The increase in $SO_4^=$ concentrations towards the west, where alkaline prairie soils rich in $CaSO_4$ and Na_2SO_4 occur, is in line with this explanation. The NH_4^+:$SO_4^=$ and NH_4^+:NO_3^- correlations also decreased from east to west. As the anthropogenic influences decrease and natural sources become more important the correlations among these ions become insignificant.

The strong correlation between Pb, which is nearly exclusively emitted by combustion of leaded gasoline (EPA 1977), and NO_3 suggests

automobile exhausts as an important source for both these elements. This correlation is greatest at Hovland and Itasca where the influence of long-range transport on precipitation is strongest. Some Pb may also be soil-derived; the Pb:Al and Pb:Fe correlation coefficients are large and increase from east to west as the influence of soil dust increases.

The correlation coefficients in event-precipitation samples, either positive or negative, between pH and the logarithms of ions expected to control it were generally small and insignificant. The partial correlations of $SO_4^=$ with pH and of NO_3^- with pH (controlled for NH_4^+ effects) did, however, have significant negative values ($r_{NO_3^-}$:pH, NH_4^+ = -0.55, $r_{SO_4^=}$:pH, NH_4^+ = -0.52) at Hovland, as would be expected if the precipitation pH was *controlled by the fraction of acids not neutralized by* NH_3. The partial correlations between pH and $SO_4^=$ or NO_3^- (controlled for NH_4^+) at Itasca and Tewaukon were also negative, but they were not significant.

The correlation coefficients among ions in the March 1978 snow core samples from northeastern Minnesota (see Table 13) indicate relationships in snow collected from a relatively local homogeneous area. Nitrate had a very large and significant negative correlation with pH (positive correlation with H^+). Sulfate was only moderately correlated with pH. Because it had a fairly large correlation coefficient with NH_4^+ it is possible that $SO_4^=$ was partially neutralized by NH_4^+ and that NO_3^- was the major acid anion. The negative correlations

between pH and the remaining ions suggest that dilution was at least as important as neutralization by alkaline materials in causing the higher pH values observed in some of the snow samples. Moreover, all the samples were below pH 5.0 so it is apparent that neutralization was of only minor importance.

The correlation coefficients presented in Table 14, among ions and particulates in the 1978-79 snow-core samples, indicate relationships that hold across the entire region. There were strong associations among the metal cations, P_{tot}, alkalinity, and particulate matter. Sulfate was strongly correlated with Ca^{++}, Mg^{++}, and Na^{+}, but not with NH_4^{+}, which is in line with its having a soil-source in the cultivated pairies. The ions correlated with particulates all had large positive correlations with pH; only NO_3^{-} and NH_4 had weak correlations with pH. This suggests that soil dusts were responsible for neutralizing acids in the snow on a regional scale. The partial correlation of pH with SO_4 (controlled for Ca^{++}, Mg^{++}, and NH_4^{+}) was significant and had a large negative value ($r = -0.60$). The partial correlation of pH with NO_3^{-} was also negative, but not as large ($r = -0.31$). Nitrate was more important than $SO_4^{=}$ in the most acid snow cores (those from the northeastern forest sites), but because it was more constant across the region than $SO_4^{=}$, the partial correlation coefficient of pH with NO_3^{-} was not as large as the partial correlation of pH with $SO_4^{=}$. Nitrate may be

associated with a relatively constant acid level across the region, with the increases in acidity from west to east being due to a decrease in alkaline dusts and a slight increase in acidic $SO_4^=$ of anthropogenic origin.

Ratios to Fe and Al

Because Fe and Al are derived primarily from the soil (Lantzy and Mackenzie 1979), the ratio of other elements to these two should be an indication of the relative importance of natural and anthropogenic sources of those other elements. The ratios of major ions and P to Fe and Al in event-precipitation samples are given in Table 15. The ratios of NO_3^-, $SO_4^=$, and NH_4^+ to Fe and Al increased appreciably from Tewaukon to Hovland, which suggests again that anthropogenic sources of these elements are important in the east. The metallic cations are less influenced by sources other than the soil. Their ratios to Fe and Al did not differ appreciably at Tewaukon and Itasca and were only slightly larger at Hovland. Magnesium, however, appeared to be enriched with respect to Fe and Al at Itasca; differences in local soils may be involved. Thornton (1981) presents enrichment factors and the ratios of trace metals to Al.

Ratios of NH_4^+ and Ca^{++} to $SO_4^=$

The ratios of NH_4^+ to $SO_4^=$ (see Table 16) follow the pH trends during the seasons and across the region. The mean annual $NH_4^+ : SO_4^=$ ratio was greatest at Tewaukon and least at Hovland, as was the case for pH. The ratios also decreased in the winter when pH was lowest. This suggests that precipitation acidity is partially controlled by the

fraction of $SO_4^=$ not neutralized by NH_4^+. At Hovland and Itasca the NH_4^+: $SO_4^=$ ratios also partially account for the pH variations between individual events, as is illustrated in Figs. 5 and 6. The correlation coefficients for the trend illustrated are 0.55 and 0.58 at Hovland and Itasca respectively. However, at Tewaukon, where soil-derived $SO_4^=$ and direct scavenging of locally emitted NH_3 may be important, the relationship between the NH_4^+: $SO_4^=$ ratio and pH, illustrated in Fig. 7, is neglibible. Above pH 5.9 the pH and NH_4^+: $SO_4^=$ ratio vary independently; consequently the correlation coefficient is insignificant. pH behaved similarly with respect to the NH_4^+: (NO_3 + $SO_4^=$) ratio, but not to the Ca^{++}: $SO_4^=$ ratio.

Unlike the situation with regard to the event samples, the NH_4^+: $SO_4^=$ ratio was not significantly correlated with pH in the 1978-79 snow-core samples. Because NH_4^+ was uniformly low in the snow cores this is not surprising. Instead of NH_4^+, Ca^{++} appeared to be the neutralizing cation in the snowpack. Figure 8 indicates that up to pH 7, pH increases with increasing Ca^{++}: $SO_4^=$ ratios. The Ca^{++}: $SO_4^=$ ratios in the most alkaline samples, which were all dirty snows from the prairie sites, were lower than would be expected from this trend. Some of the $SO_4^=$ in these samples may have been balanced by Na^+, which also had high concentrations in these samples. Even with these high pH points included the correlation coefficient for this trend was 0.50 and is consistent with neutralization of acids in snow after it has fallen by windblown alkaline dusts. The pH variations in the 1978 snow samples were too small to exhibit any relationship to NH_4^+: $SO_4^=$ or Ca^{++}: $SO_4^=$ ratios.

DISCUSSION

Geographic Comparisons

Table 17 presents mean annual concentrations of major ions in precipitation at various locations in North America and Scandinavia. When available I used wet-only data, but for some locations only bulk precipitation data were available and these were used. Concentrations of the soil elements Ca^{++}, Mg^{++}, Na^{+}, and K^{+} are generally higher and acidity is lower in bulk precipitation than in wet-only precipitation (Galloway and Likens 1978).

Precipitation at the sites with the most severe acid precipitation, Muskoka-Haliburton, New York, and the Los Angeles basin, is 5 times more acid than at Hovland. Precipitation at Hovland was slightly less than the range of acidities observed in southern Norway. Precipitation pH at Itasca was comparable to that in the ELA of adjacent northwestern Ontario. Sulfate concentration at Hovland was within the range of $SO_4^{=}$ concentrations observed in southern Norway, but less than at the other sites listed in table 17. Ammonium concentrations were highest at Tewaukon and the Iowa sites, which are all in the agricultural mid-western United States. Ammonium concentrations at Itasca and Hovland were comparable to those in Muskoka-Haliburton, upstate New York, Los Angeles,

and parts of southern Norway, but were greater than those in the southeastern United States, along the Atlantic coast, in the ELA, and in the majority of the Norwegian sites. This is in line with the midwest being the primary source for NH_3 emissions in the United States. The only regions with Ca^{++} concentrations comparable to those at Tewaukon were Tennessee and upstate New York, but data from both those areas were for bulk precipitation, and wet-only precipitation may not have had Ca^{++} concentrations as high. Calcium concentrations at Itasca were comparable to those at Muskoka-Haliburton and New-Jersey; Ca^{++} concentrations at Hovland were comparable to those in the ELA, New York City, and Florida. Calcium concentrations at the remaining sites listed in Table 17 were appreciably less than at any of the sites in this study. Distance from sources of calcareous dust, either urban areas or agricultural regions, appears to be an important factor controlling Ca^{++} concentrations at the sites considere here.

Concentrations of major ions during the period July 1978 to June 1979 at the Marcell Minnesota site in the NADP network, which is located in north central Minnesota 130 km ENE of Itasca (NADP 1978, 1979), are generally comparable to or intermediate to the concentrations at Itasca and Hovland. However, NH_4^+ is higher in the event samples from Itasca and Hovland than in samples from Marcell. NH_4 may have been lost from the NADP samples, which are collected

weekly, but not from the samples in this study, which are collected on an event basis. Alternatively, samples in this study may have gained NH_4^+ during storage prior to analysis. The concentrations of H^+ at Marcell were intermediate to the concentrations at Itasca and Hovland.

Precipitation collected during only one year may not represent adequately the long-term conditions at a site (Likens et al. 1977). I compared the data from this study with studies during the 1950s by Junge (Junge and Gustafson 1957, Junge and Werby 1958, Junge 1963) and found reasonably good agreement fot the concentrations of Na^+, K^+ and $SO_4^=$ in precipitation over this region. Chloride was substantially less in Junge's studies than in event precipitation samples from this study. Calcium concentrations in Junge's studies were comparable to Ca^{++} concentrations at Tewaukon, but appeared not to follow as steep a decline from west to east across the north-central United States during the 1950s. However, Junge did not have a site near the Hovland site. Concentrations of NO_3^- were somewhat greater in this study than in the 1950s and NH_4^+ concentrations were dramatically greater. Increases in populations of livestock and applications of fertilizer on the cultivated prairie could well explain the increase in NH_4^+ concentrations. Emissions of NO_x have been increasing steadily since the 1950s (US EPA 1976) and it is therefore likely that NO_3^- in precipitation has increased in this region.

Ecological Aspects of Atmospheric Deposition in Minnesota

Atmospheric inputs may have a number of effects on ecosystems

in Minnesota and the surrounding region. Nutrients in precipitation may constitute a significant portion of the nutrient budgets for lakes, wetlands, and perhaps some forests. Rawson Lake, an oligotrophic lake in the ELA that is similar to many lakes in adjacent northeastern Minnesota and northern Wisconsin, received up to 50% of its annual N and P inputs directly from the atmohspere (Schindler et al. 1976). Eighty two percent of the P_{tot} input to Dogfish Lake, a small oligotrophic lake with an undisturbed watershed in northeastern Minnesota, was supplied by precipitation during 1972 (Tarapchak and Wright 1977). Annual deposition of N and P at Hovland and Itasca are comparable to deposition values at Rawson Lake and Dogfish Lake, so atmospheric inputs of these nutrients to oligotrophic lakes in undistrubed watersheds are probably as important throughout the forested region of Minnesota, Wisconsin and adjoining Ontario.

Concentrations of major ions and nutrients in 15 dilute lakes of northeastern Minnesota and northern Wisconsin, which had ion balances between 0.90 and 1.10, are compared with mean annual precipitation concentrations at Itasca and Hovland in Table 18. Inorganic N in precipitation was 10 times greater than it was in the lakes; P was approximately equal in Itasca precipitation and in the lakes. If the plant-derived P that was important during the spring at Hovland is included then precipitation P is often greater than P concentrations in oligotrophic lakes. The concentrations of the major cations and $SO_4^=$ were 2 to 10-fold

greater in the lake water than in precipitation. These differences could be due partly to inputs from dry fallout and weathering, and partly to losses of water by evaporation. Calcium, Mg^{++}, and K^{+}, which are most enriched in lake water relative to precipitation, are present in soil and most likely to be added by leaching or dry deposition.

Large areas of northern Minnesota are covered with peatlands, where the vegetation is dependent entirely on the atmosphere for its nutrients. As noted previously, the mineral content of Sphagnum is greater in western than in eastern Minnesota. Tilton (1977) noted that the growth of tamarack (Larix larcina) in three wetland ecosystems was positively correlated to the supply of N and P (as indicated by foliar concentrations of these elements). It is also probable that atmospheric inputs of N may be important to upland forests in the region, especially those growing on shallow soils overlying resistant bedrock or soils derived from coarse sandy parent material. In simulated acid-rain studies pine seedling growth -- as indicated by needle length and dry weight -- was greater in pots watered with acid solutions containing HNO_3 (Wood 1976).

In the long run, however, the beneficial effects of nutrients in precipitation are likely to be overcome by deleterious effects of the acids that often accompany them. Nutrient leaching, trace-metal mobilization, acceleration of natural soil acidification, and alteration of nutrient mineralization processes are potential terrestrial effects of acid precipitation

(McFee 1978, Tamm 1976). These effects are most likely to occur in northeastern Minnesota, adjoining Ontario, and northern Wisconsin, where shallow, non-calcareous glacial deposits overlie resistant crystalline bedrock and acid inputs are highest. In addition, Reuss (1975) points out that NH_4^+ has a potential to acidify soils through biological processes. Thus, even where anthropogenic acids in precipitation are neutralized by NH_3, the potential damaging affects may not be alleviated. Nevertheless, the input of other alkaline bases Ca^{++} and Mg^{++} -- generally balanced by HCO_3 -- may temper the acidifying effects on soils. The net effect may not be apparent for several decades, as the changes expected to take place in sensitive soils are slow to occur. It should be noted that for many coarse sandy soils, acidification is a slow natural process that can be greatly accelerated by acid precipitation.

The most imminent effects of acid precipitation are lake acidification and associated changes in species composition and abundance at all trophic levels. The geology of those portions of northeastern Minnesota, adjoining Ontario, and northern Wisconsin where precipitation is most acid is similar to the geology in areas, such as Scandinavia, the Adirondacks, southern Ontario, and Nova Scotia where these effects have been observed (Glass and Loucks 1980). Kramer (1979) reported that numerous lakes in and around Quetico Provincial Park, which abuts the Boundary Waters Canoe Area Wilderness in northeastern Minnesota and is in the same drainage basin, had Calcite

Saturation Indices (CSI) greater than 3, which indicate susceptibility to acidification. Recent surveys of pH and alkalinity in the lakes of northeastern Minnesota and northern Wisconsin (Glass and Loucks 1980, Eilers et al. 1979) indicate that many of them, especially in Wisconsin, have very low alkalinities and that some may already have reached pH levels critical to organisms (cf Fig. 9). However, the pH and alkalinity values of the Minnesota and Wisconsin lakes are not as low as those of the most severely affected lakes in Norway and the Adirondacks.

Spring snow melt is especially critical for aquatic ecosystems; the eggs and juvenile stages of many organisms that occur during spring are more sensitive to acid than the adults are. Furthermore, influxes of acid from melting snow may cause the pH in streams and surface layers of lakes to decrease temporarily, even in waters of moderately higher alkalinity (Galloway et al. 1980). Haapala et al. (1975) reported that pH in the Kiiminkijoki River decreased from near 6.5 to 5.0 during the melting of snow with a pH of 4.5, -- comparable to snow in much of northeastern Minnesota. Jeffries et al. (1979) reported spring pulses of acid in Ontario lakes and streams from melting of snow at pH 4.0 - 4.5. Even if Minnesota and Wisconsin lakes and streams do not become permanently acidified, they may experience acid pulses during snowmelt that could affect the biota adversely.

SUMMARY AND CONCLUSIONS

The supply of alkaline soil dust and gaseous NH_3 available to neutralize anthropogenic acids in the atmosphere controls the western extent of acid precipitation. The acidity of wet precipitation increased 4-fold from west to east across North Dakota and Minnesota as the amount of alkaline dust and NH_3 decreased with increasing distance from their sources in the cultivated prairie. Calcium and Mg^{++} concentrations decreased 2 to 3-fold from west to east. However, minimum concentrations of NH_4^+ and $SO_4^=$ were observed at Itasca, the central site. Natural emissions of these elements were important in the west, while anthropogenic emissions were responsible for the higher concentrations in the east. Wet deposition of H^+ decreased 8-fold and deposition of NO_3^- and $SO_4^=$ decreased 1.5 to 2-fold from Hovland in the east to Tewaukon in the west. Wet deposition of the metal cations increased from Hovland to Tewaukon. Dry deposition followed the same trend.

Winter snow cover and freezing temperatures, which decreased airborne soil dust and the evolution of NH_3 from the prairie soils, led to an increase in precipitation acidity at all sites. The acid increase was accompanied by a decrease in alkaline metal cations, especially Ca^{++}, and in NH_4^+. At Hovland $SO_4^=$ and NO_3^- also increased during the winter. The occurrence of snow events at Tewaukon that were appreciably more acid than the snowpack accumulated

there indicates that snow was neutralized after it fell by alkaline dust entrained in resuspended snow or deposited separately. Winter inputs of acid are especially important because they are released during a short period in the spring. Over half of the acid input at Hovland occurred during the winter.

Precipitation inputs of P and N probably have significant beneficial effects on nutrient-poor eocsystems in Minnesota and surrounding areas. However, acid precipitation at Hovland is approaching levels known to cause adverse effects in sensitive regions. The geology of northeastern Minnesota, adjoining Ontario, and northern Wisconsin is similar to that in areas where lake acidification and losses of fish populations have occurred, so that such problems may eventually occur in central North America. Any increase in acid loading because of the development of more coal-fired power plants or a copper-nickel smelter in the region, or relaxation of SO_x and NO_x emission standards throughout the United States, will increase this danger.

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Table 1. Geometric mean concentrations and number of analyses (n) for major ions, total phosphorus, trace metals†, particulates > 0.4 μm, specific conductivity, and specific conductivity adjusted for the contribution due to H^+ in event-precipitation samples collected at the three collector sites from 15 April 1978 to 30 June 1979. Major ions are given in μeq ℓ^{-1}, total phosphorus and trace metals are in μg ℓ^{-1}, particulates > 0.4 μm are in dry-weight mg ℓ^{-1} and specific conductivity is in μS corrected to 25° C. Order from high to low and significant differences are indicated. (See text for explanation of superscripts).
T= Tewaukon, I= Itasca, H= Hovland.
† Data from Thornton (1980)

	TEWAUKON mean (n)	ITASCA mean (n)	HOVLAND mean (n)	ORDER hi.....low
H^+	1.92 (47)	4.2 (79)	17.8 (81)	H^a I^b T^c
pH	5.79	5.38	4.75	
Na^+	10.0 (47)	7.8 (76)	6.5 (75)	T^a I^b H^b
K^+	4.9 (47)	3.1 (75)	2.6 (75)	T^a I^b H^b
NH_4^+	36.4 (36)	22.1 (67)	20.7 (65)	T^a I^b H^b
Ca^{++}	44.0 (38)	30.5 (74)	19.0 (69)	T^a I^b H^c
Mg^{++}	17.5 (44)	13.3 (74)	7.5 (71)	T^a I^a H^b
Cl^-	31.0 (46)	35.2 (73)	23.7 (71)	I^a T^a H^a
NO_3^-	26.4 (47)	19.3 (77)	22.1 (75)	T^a H^{ab} I^b
$SO_4^=$	33.8 (47)	26.9 (77)	40.0 (75)	H^a T^{ab} I^b
P_{tot}	19.0 (42)	10.5 (70)	9.3	T I H**
Al	139 (22)	56.1 (41)	32.1 (36)	T I H**
Fe	100.0(23)	30.6 (40)	21.8 (36)	T I H**
Mn	11.7 (23)	3.67 (39)	1.94 (35)	T I H**
Pb	6.71 (23)	4.69 (40)	6.46 (35)	T H I^o
Zn	83.8 (23)	54.6 (41)	65.3 (36)	T H I^o
Cd	.34 (22)	.15 (41)	.15 (35)	T I ≈ H**
Cr	<.36 (20)	<.25 (40)	<.28 (35)	T H I^o
Ni	2.16 (22)	<1.11(40)	<.88 (35)	T I H**
Cu	2.11 (21)	1.09 (41)	1.46 (35)	T H I^o
Part.	12.4 (24)	6.5 (42)	5.6 (29)	T I H**
Cond.	19.0	16.5 (79)	22.6 (81)	H^a T^{ab} I^b
Cond.($-H^+$)	16.8 (47)	12.8 (79)	13.3 (81)	T^a H^{ab} I^b

* $p < .05$
** $p < .01$
o differences not significant

Table 2. Ranges and volume-weighted mean concentrations of major ions, total phosphorus, and trace metals† in event-precipitation samples collected at the three collector sites from 15 April 1978 to 30 June 1979. Major ion concentrations are in $\mu eq\ \ell^{-1}$ and total phosphorus and trace metals are in $\mu g\ \ell^{-1}$. Order of concentrations from high to low and significant differences are indicated as in Table 1.

T = Tewaukon, I = Itasca, H = Hovland.

† Data from Thornton (1981)

	TEWAUKON			ITASCA			HOVLAND			ORDER
	mean	range	(n)	mean	range	(n)	mean	range	(n)	hi - lo
pH	5.27	4.21-7.42	(47)	5.00	4.33-6.88	(79)	4.67	3.61 - 6.77	(81)	T I H
H^+	5.4	.038-61.7	(47)	10.0	.132-37	(79)	21.5	.170 - 246.	(81)	H^a I^b T^c
Na^+	11.7	1.7-77.	(47)	8.7	1.7-456.	(76)	6.1	1.3 - 72.	(75)	T^a I^{ab} H^b
K^+	5.9	1.0-33.1	(47)	4.4	0.5-111	(75)	3.3	≤0.3 - 21	(75)	T^a I^{ab} H^b
NH_4^+	47.9	1.4-124.	(36)	33.6	≤1.4-179	(67)	37.1	≤1.4 - 205.	(65)	T^a H^{ab} I^b
Ca^{++}	52.5	7.5-211.	(38)	34.5	3.0-286	(74)	20.0	3.0 - 197.	(69)	T^a I^b H^c
Mg^{++}	22.5	1.7-118.	(44)	19.2	1.3-258	(74)	10.8	≤.2 - 148	(71)	T^a I^{ab} H^b
Cl^-	49.9	5.4-256	(46)	46.8	5.1-383	(73)	26.2	2.8 - 732	(71)	T I H
NO_3^-	25.7	4.3-133.	(47)	20.0	4.3-79.3	(77)	20.7	3.6 - 260	(75)	T^a H^a I^a
$SO_4^=$	36.3	4.4-229.	(47)	31.9	6.3-158	(77)	39.4	3.8 - 315	(75)	H^a T^a I^a
P_{tot}	32.9	2.0-600.	(42)	14.2	≤1-189	(70)	28.9	≤1. - 611	(70)	T^a H^{ab} I^b
Part	21.1	0.8-125.	(25)	6.7	N.D. 29	(46)	4.6	N.D - 24.7	(39)	T I H
Cond	19.3	5.7-60.1	(47)	16.2	49-55.2	(79)	20.3	4.1-159.5	(81)	H T I
Cond ($-H^+$)	17.4	4.5-59.9	(47)	12.7	3.7-55.1	(79)	12.8	1.9-96.9	(81)	T H I
Fe	165.	7.43-669.		50.5	1.0-189		38	4.15 -449		T I H
Mn	22.	1.97-66.8		5.6	0.20-47.1		3.2	0.13 -22.4		T I H
Pb	8.	1.33-39.9		5.7	0.80-13.3		7.1	0.80 -18.9		T H I
Zn	147.	0.3-535		95.	3.18-673		90	9.60 -873		T I H
Cd	.73	0.03-3.15		.18	≤0.02-1.60		.15	≤0.02 -2.01		T I H
Cr	.40	≤0.20-1.26		.20	≤0.20-1.85		.15	≤0.20 -2.68		T I H
Ni	3.6	≤0.50-29.1		1.4	≤0.50-15.6		1.3	≤0.50 -5.09		T I H
Cu	3.9	≤0.20-13.5		2.1	≤0.20-19.5		3.5	≤0.20 -16.7		T H I

Table 3. Ranking of major ions at the three collector sites.

Ranking	Tewaukon	Itasca	Hovland
Cations			
1	Ca^{++}	Ca^{++}	NH_4^+
2	NH_4^+	NH_4^+	H^+ *
3	Mg^{++}	Mg^{++}	Ca^{++} *
4	Na^+	H^+	Mg^{++}
5	K^+	Na^+	Na^+
6	H^+	K^+	K^+
Anions			
1	Cl^-	Cl^-	$SO_4^=$
2	$SO_4^=$	$SO_4^=$	Cl^-
3	HCO_3^-	NO_3^-	NO_3^-
4	NO_3^-	HCO_3^-	HCO_3^-

* H^+ and Ca^{++} were equal

Table 4. Estimated annual wet deposition of major ions, total phosphorus and trace metals* at the three collector sites. Ion depositions are in meq m^{-2} yr^{-1}, total phosphorus and trace metals are in mg m^{-2} yr^{-1}, and H_2O deposition is in ℓ m^{-2} yr^{-1} (mm yr^{-1}). Sites are ordered from highest to lowest.

* Data from Thornton (1981)

	Tewaukon	Itasca	Hovland	Order hi----low
H^+	2.1	6.7	16.4	H I T
Na^+	5.1	6.3	4.6	I T H
K^+	2.7	2.5	2.2	T I H
NH_4^+	17.9	21.1	23.1	H I T
Ca^{++}	20.9	21.6	16.2	I T H
Mg^{++}	9.2	13.2	8.2	I T H
NO_3^-	10.8	13.3	15.2	H I T
$SO_4^=$	13.0	19.8	26.8	H I T
P_{tot}	13.3	9.2	15.0	H T I
Al	101.	69.3	39.3	T I H
Fe	66.8	34.0	26.7	T I H
Mn	8.9	3.77	2.25	T I H
Pb	3.2	3.83	4.98	H I T
Zn	59.5	63.9	63.2	I H T
Cd	0.296	0.121	0.105	T I H
Cr	0.162	0.135	0.105	T I H
Ni	1.46	0.942	0.913	T I H
Cu	1.58	1.41	2.46	H T I
H_2O	405.1	672.8	702.1	H I T

Table 5a. Dry deposition of major ions at the three collector sites during spring 1979. Depositions are expressed in terms of meq m^{-2} per quarter (3 months). P_{tot} is expressed in mg m^{-2} $quarter^{-1}$. pH is of a 250 ml suspension of particulate matter.

	Tewaukon	Itasca	Hovland
Na^+	0.30	0.09	0.16
K^+	0.22	0.13	0.14
NH_4^+	0.71	0.37	0.79
Ca^{++}	3.42	2.19	1.26
Mg^{++}	0.99	2.21	0.53
Cl^-	0.48	1.75*	0.17
NO_3^-	1.00	0.60	0.68
$SO_4^=$	2.34	1.08	1.79
P_{tot}	2.9	0.36	1.3
pH_{250ml}	6.5	6.1	5.1

* Apparent high Cl^- deposition due to one exceptional sample.

Table 5b. Days sampled, number of samples, and mean dry deposition (± standard error) of major ions, total phosphorus, and total mass. Ion depositions are in meq m^{-2} yr^{-1} and total mass is in g m^{-2} yr^{-1}. pH values are for 250-ml suspensions of particulate matter.

	Tewaukon				Itasca				Hovland			
	mean	std err	n	days sampled	mean	std err	n	days sampled	mean	std err	n	days sampled
Na^+	1.04	.23	3	95	.76	.19	5	163	.93	.22	8	245
K^+	1.08	.30	3	95	1.65	.48	6	198	2.4	.63	9	275
NH_4^+	15.9	13.1	3	113	7.8	2.9	6	187	2.5	1.08	4	123
Ca^{++}	13.8	.33	3	95	7.7	1.2	7	248	4.6	.94	7	181
Mg^{++}	3.8	.39	3	95	6.5	2.3	7	170	1.7	.23	8	211
Cl^-	1.9	.84	2	61	6.2*	3.2	4	148	1.1	.12	5	189
NO_3^-	4.0	1.98	2	61	1.8	.70	4	148	2.4	.33	5	189
$SO_4^=$	9.3	5.2	2	61	3.6	1.5	4	148	5.8	1.46	5	189
P_{tot}	13.0	5.3	2	61	9.2	3.3	7	205	8.9	4.55	6	204
Total mass	6.3	1.6	2	61	3.7	1.9	5	175	3.1	.53	5	189
$pH_{2\,50ml}$	6.53	-	2	61	6.45	.45	6	198	5.55	.48	4	151

* apparent high concentration due to high Cl^- in sample collected on 14 May 1979. Dry depostion = 3.3 meq m^{-2} yr^{-1} if that sample is excluded from the calculations

Table 6. Volume-weighted mean concentrations of major ions during the four seasons of 1978-79. Numbers in parentheses indicate the ranking of ions. For each site ions are ordered according to their ranking in mean annual precipitation. Ion concentrations are in meq ℓ^{-1}, total P is in $\mu g\ \ell^{-1}$ and H_2O is in $\ell\ m^{-2}$.

	Spring		Summer		Fall		Winter		Spring	
				Tewaukon						
Ca^{++}	48.0	(2)	72	(1)	169	(1)	32	(1)	28	(2)
NH_4^+	51	(1)	49	(2)	62	(2)	18	(3)	54	(1)
Mg^{++}	21	(3)	22	(3)	35	(3)	24	(2)	17	(3)
Na^+	14	(4)	14	(4)	16	(5)	10	(5)	5	(4)
K^+	5	(6)	8	(5)	22	(4)	2	(6)	5	(5)
H^+	5.8	(5)	2.7	(6)	.15	(6)	13.8	(4)	3.5	(6)
Cl^-	50	(1)	65	(1)	22	(4)	58	(1)	13	(4)
$SO_4^=$	36	(2)	32	(3)	54	(2)	32	(2)	39	(1)
HCO_3^-	22	(4)	35	(2)	137	(1)	.4	(4)	23	(3)
NO_3	24.	(3)	22	(4)	34	(3)	31	(3)	29	(2)
P_{tot}	29.5		27.9		150.5		15.3		30.5	
H_2O	-		125.4		23.8		68.1		118.0	
				Itasca						
Ca^{++}	119	(1)	24	(2)	27	(1)	25	(2)	28	(3)
NH_4^+	54	(2)	31	(1)	11	(2)	14	(4)	42	(1)
Mg^{++}	29	(3)	8	(4)	11	(4)	26	(1)	29	(2)
H^+	10	(4)	10	(3)	11	(3)	18	(3)	7	(4)
Na^+	15	(5)	6	(5)	10	(5)	4	(5)	6	(5)
K^+	12	(6)	2	(6)	8	(6)	3	(6)	5	(6)
Cl^-	97	(1)	39	(2)	47	(1)	39	(1)	30	(2)
$SO_4^=$	49	(2)	24	(3)	20	(2)	20	(3)	46	(1)
HCO_3^-	13	(4)	226	(1)	.5	(4)	0	(4)	12	(4)
NO_3	30	(3)	16	(4)	17	(3)	21	(2)	21	(3)
P_{tot}	19.7		12.2		20.9		8.3		15.1	
H_2O	-		336.1		62.8		96.4		213.9	
				Hovland						
NH_4^+	50	(1)	21	(2)	50	(1)	29	(2)	42	(1)
H^+	17	(2)	14	(3)	19	(3)	58	(1)	12	(4)
Ca^+	14	(3)	24	(1)	34	(2)	21	(3)	14	(3)
Mg^{++}	7	(4)	8	(4)	6	(5)	7	(5)	22	(2)
Na^+	6	(5)	6	(5)	10	(4)	8	(4)	3	(6)
K^+	5	(6)	2	(6)	3	(6)	2	(6)	5	(5)
$SO_4^=$	49	(1)	26	(2)	39	(2)	57	(1)	36	(1)
Cl^-	30	(2)	34	(1)	44	(1)	28	(3)	8	(3)
NO_3^-	17	(3)	15	(3)	24	(3)	39	(2)	18	(2)
HCO_3^-	8	(4)	0	(4)	7	(4)	0	(4)	0	(4)
P_{tot}	49.7		8.9		15.0		4.8		52.7	
H_2O	-		244.1		94.2		137.4		240.8	

Table 7. Seasonal deposition of major ions and P_{tot} during the four seasons of 1978-79. All values are in meq m^{-2} for a 3-month period, except P_{tot} which is in mg m^{-2} for a 3-month period.

	Summer	Fall	Winter	Spring
TEWAUKON				
H^+	0.34	0.004	0.94	0.42
Na^{++}	1.74	0.38	0.68	0.61
K^+	0.99	0.52	0.16	0.54
NH_4^+	6.09	1.47	1.22	6.40
Ca^{++}	6.02	4.01	2.21	3.24
Mg^{++}	2.61	0.83	1.65	1.97
Cl^-	8.2	0.53	3.92	1.56
NO_3^-	2.77	0.80	2.14	3.37
$SO_4^=$	4.00	1.29	2.21	4.58
HCO_3	4.39	3.25	0.03	2.71
P_{tot}	3.5	3.8	1.0	3.6
ITASCA				
H^+	3.29	0.69	1.74	1.42
Na^+	2.05	0.60	0.41	1.22
K^+	0.69	0.50	0.32	0.99
NH_4^+	10.32	0.71	1.38	9.01
Ca^{++}	7.9	1.70	2.41	5.89
Mg	2.8	0.68	2.49	6.24
Cl^-	13.1	2.95	3.78	6.50
NO_3^-	5.52	1.08	2.06	4.59
$SO^=$	7.98	1.26	1.93	9.75
HCO_3^-	76.0	0.03	0.0	2.57
P_{tot}	4.1	1.3	0.80	3.2
HOVLAND				
H^+	3.46	1.84	7.96	2.94
Na^+	1.49	0.94	1.13	0.63
K^+	0.56	0.32	0.21	1.11
NH_4^+	5.06	4.72	3.92	10.15
Ca^{++}	5.98	3.21	2.89	3.49
Mg^{++}	1.83	0.55	0.92	5.22
Cl^-	8.32	4.15	3.92	1.90
NO_3^-	3.66	2.23	5.40	4.3
$SO_4^=$	6.41	3.66	9.62	8.73
HCO_3^-	0.0	0.66	0.0	0.0
P_{tot}	2.17	1.42	0.66	12.7

Table 8. Specific conductivity and concentrations of major ions, P_{tot}, and particles in snow cores collected during mid-March in northeastern Minnesota. Conductivity and conductivity corrected for the contribution due to H^+ are expressed in μS at 25° C, concentrations of major ions are in μec l^{-1} and P_{tot} and particle concentrations are in μg l^{-1} and mg l^{-1} respectively.

	all data		(n= 8) vertical cores		(n= 8) surface fresh		(n= 10) old bottom		(n= 11) intermediate		(n= 5) icy crusts	
	geo. mean	range	mean	std. err.	mean	std. err.	mean	std. err.	mean	std. err.	mean	std. err.
Cond.	10.8	(5.3-22.4)	11.7	.58	8.1	.88	8.7	.57	15.9	1.3	12.7	1.8
$Cond_{(H^+)}$	4.4	(2.0-11.9)	4.8	.36	3.5	.59	4.1	.26	6.1	.97	5.4	.43
H^+	17.7	(9.3-38.9)	20.0	1.0	12.9	.98	13.4	1.4	28.1	1.9	20.9	4.2
Na^+	6.1	(2.2-36.1)	6.5	.77	7.0	1.6	5.7	.90	11.3	3.0	5.7	1.1
K^+	3.1	(1.3-9.0)	4.4	.69	2.8	.58	3.6	.74	3.6	.64	3.1	.77
NH_4^-	7.9	(0.7-40.)	9.3	1.9	10.0	2.5	10.0	2.2	11.4	3.6	9.3	3.1
Ca^{++}	8.0	(1.0-5.7)	8.0	1.2	10.0	6.7	15.0	3.5	13.0	4.4	11.0	2.4
Mg^{++}	1.5	(0.1-8.1)	2.3	.27	1.0	.36	2.3	.36	1.8	.45	4.6	1.3
Cl^-	6.8	(0.85-69)	7.0	1.1	7.6*	—	11.8	3.6	12.4	3.9	4.2	.98
NO_3^-	16.4	(7.1-41.4)	17.1	1.1	11.4	1.3	14.3	.89	26.4	2.4	20.0	3.2
$SO_4^=$	14.4	(5.0-27.5)	17.5	1.4	11.9	2.6	14.4	1.6	16.3	2.1	20.0	2.(
P_{tot}	7.2	(1.2-45.3)	11.0	2.7	2.8	.60	11.4	4.0	10.8	1.6	14.9	4.2
Part.	6.3	(0.0-82)	7.5	1.2	4.1	.80	14.4	8.6	9.0	2.6	19.2	7.2

Table 9. Standard error and mean concentration of major ions, total P, particulates, and specific conductivity in snow core samples collected during winter 1978-79 grouped according to local vegetation cover. Major ions are in μeq ℓ^{-1}, total P is in μg ℓ^{-1}, particles are in mg ℓ^{-1} and specific conductivity is in μ S corrected 25° C.

	Prairie		Transition Forest		Northeastern Forest	
	mean	std err.	mean	std err.	mean	std err.
pH	6.68	.25	5.52	.26	4.53	.03
H^+	0.2	-	3.0	-	29.5	-
Na^+	89.1	55.2	7.0	1.7	4.8	1.3
K^+	9.7	2.6	6.4	2.8	1.8	.3
NH_4^+	17.9	3.3	13.6	1.6	13.6	1.9
Ca^{++}	103.0	24.0	21.0	4.0	9.5	1.3
Mg^{++}	63.3	23.7	28.3	17.8	3.3	1.6
Cl^-	25.4	13.6	7.6	1.7	6.5	1.5
NO_3^-	60.7	29.1	26.4	2.9	28.6	1.9
$SO_4^=$	162.5	59.3	18.1	1.5	23.8	2.7
HCO_3^-	52.	23.	30.	22.	0.	-
P_{tot}	79.6	23.7	14.5	2.1	9.2	1.7
Particles >0.4 μm	39.3	12.6	12.2	6.5	6	1.7
Cond	73.8	42.6	13.1	1.8	17.0	1.1
H_2O	138*	15	92	1.6	172	43.

*Calculated from samples collected in sites where snow was deposited. Not an accurate estimate of snow depth at all sites of the prairie.

Table 10. Correlation matrices of major ions and trace metals for precipitation collected at Tewaukon. Coefficients were computed from logarithms of concentration. Asterisks denote significance level; *p<.05 **p<.01

	Ca^{++}	Mg^{++}	Al	Fe	Mn	Na^{+}	K^{+}	P_{tot}	NH_4^{+}	$SO_4^{=}$	NO_3^{-}	Ni	Pb	Zn	Cd	Cr	Cu	Cl^{-}	pH
Ca^{++}	1.0																		
Mg^{++}	.70**	1.0																	
Al	.38	.52*	1.0																
Fe	.36	.52*	.84**	1.0															
Mn	.60**	.43*	.82**	.78**	1.0														
Na^{+}	.70**	.43**	.21	.15	.29	1.0													
K^{+}	.65**	.50**	.46*	.38	.72**	.57**	1.0												
P_{tot}	.51**	.44**	.45*	.49*	.70**	.28	.71**	1.0											
NH_4^{+}	.08	.19	.28	.26	.44	.21	.25	.17	1.0										
$SO_4^{=}$	.28	.49**	.23	.13	.39	.25	.43**	.40**	.47**	1.0									
NO_3^{-}	.34*	.29	.59**	.54**	.65**	.25	.43**	.47**	.28	.61**	1.0								
Ni	.24	.40	.42	.43*	.35	.46*	.38	.03	.43	.39	.32	1.0							
Pb	.07	.35	.66**	.59**	.48*	.27	.24	.16	.30	.39	.64**	.65**	1.0						
Zn	.25	.25	-.06	-.06	-.03	.33	.09	.31	.09	.18	.12	.22	.06	1.0					
Cd	.39	.38	.21	.05	.17	.56**	.24	.12	.09	.25	.17	.19	.28	.28	1.0				
Cr	.25	.53*	.38	.45*	.55*	.49*	.41	.34	.05	.22	.59**	.31	.61**	-.08	.19	1.0			
Cu	.24	.62**	.32	.36	.38	.44*	.53*	.28	.19	.29	.21	.41	.35	.08	.50*	.39	1.0		
Cl^{-}	.39*	.49**	-.33	-.32	-.31	.60**	.26	-.08	-.04	.04	-.09	.14	-.11	.13	.53*	.08	.40	1.0	
pH	.23	.36*	.19	.21	.38	.06	.49**	.53**	.29	.39**	-.02	.04	-.14	-.22	-.12	.03	.26	-.04	1.0

Table 11. Correlation matrices of major ions and trace metals for precipitation collected at Itasca. Coefficients were computed from logarithms of concentration. Asterisks denote significance level; *p<.05 **p<.01

	Ca^{++}	Mg^{++}	Al	Fe	Mn	Na^{+}	K^{+}	P_{tot}	NH_4^{+}	$SO_4^{=}$	NO_3^{-}	Ni	Pb	Zn	Cd	Cr	Cu	Cl^{-}	pH
Ca^{++}	1.0																		
Mg^{++}	.61**	1.0																	
Al	.60**	.28	1.0																
Fe	.57**	.22	.79**	1.0															
Mn	.66**	.41**	.76**	.83**	1.0														
Na^{+}	.58**	.36**	.45**	.39*	.53**	1.0													
K^{+}	.36**	.21	.16	.34*	.42**	.56**	1.0												
P_{tot}	.37**	.05	.50**	.53**	.66**	.24*	.38**	1.0											
NH_4^{+}	.33**	.15	.62**	.62**	.69**	.08	.03	.25	1.0										
$SO_4^{=}$	.28*	.28*	.48**	.46**	.57**	.14	.19	.22	.69**	1.0									
NO_3^{-}	.47**	.23*	.45**	.47**	.66**	.18	.32**	.46**	.46**	.63**	1.0								
Ni	.45**	.47**	.37*	.35*	.39*	.32*	.24	.09	.25	.45**	.37*	1.0							
Pb	.36*	.08	.46**	.42**	.46**	.11	.19	.23	.37*	.55**	.72**	.27	1.0						
Zn	.39*	.46**	.24	.06	.25	.65**	.02	.21	.14	.09	-.05	.18	-.18	1.0					
Cd	.49**	.38*	.31*	.17	.41**	.53**	.33*	.19	.17	.12	.19	.06	.16	.39*	1.0				
Cr	.38*	.24	.28	.17	.36*	.34*	.15	.12	-.03	.14	.29	.39*	.38*	.12	.36*	1.0			
Cu	.11	.02	.12	.02	-.04	.29	.01	.09	-.26	-.17	-.20	.22	-.12	.41**	.10	.39	1.0		
Cl^{-}	.62**	.59**	.37*	.23	.41*	.48**	.31**	-.01	.07	.20	.17	.44**	.07	.60**	.51**	.34*	.15	1.0	
pH	.27*	.29*	.49**	.54**	.62**	.19	.22	.42**	.53**	.32**	.20	.27	.04	.14	-.05	.17	-.15	.18	1.0

Table 12. Correlation matrices of major ions and trace metals for precipitation collected at Hovland. Coefficients were computed from logarithms of concentration. Asterisks denote significance level; *p<.05 **p<.01

	Ca^{++}	Mg^{++}	Al	Fe	Mn	Na^{+}	K^{+}	P_{tot}	NH_4^{+}	$SO_4^{=}$	NO_3^{-}	Ni	Pb	Zn	Cd	Cr	Cu	Cl^{-}	pH
Ca^{++}	1.0																		
Mg^{++}	.62**	1.0																	
Al	.59**	.61**	1.0																
Fe	.42*	.50**	.87**	1.0															
Mn	.52**	.52**	.72**	.77**	.1.0														
Na^{+}	.66**	.49**	.25	.17	.41*	1.0													
K^{+}	.33**	.41**	.35*	.30	.32	.24*	1.0												
P_{tot}	.11	.29*	.38*	.58**	.54**	-.12	.60**	1.0											
NH_4^{+}	.09	.22	.21	.31	.27	.01	.39**	.53**	1.0										
$SO_4^{=}$	.25*	.33**	.32	.36*	.41*	.24*	.32**	.39**	.64**	1.0									
NO_3^{-}	.24	.17	.32	.35*	.38*	.37**	.20	.20	.58**	.68**	1.0								
Ni	.07	.12	.21	.31	.38*	-.11	.08	.32	.09	.06	.05	1.0							
Pb	.32	.18	.44**	.37*	.39*	.35*	.24	.17	.53**	.72**	.71**	.05	1.0						
Zn	.80**	.38*	.20	.09	.26	.72**	.11	-.06	-.12	.09	.07	-.05	.14	1.0					
Cd	.67**	.60**	.57**	.44**	.50**	.72**	.35*	.14	.04	.32	.28	.05	.48**	.52**	1.0				
Cr	.23	.17	.33*	.27	.17	.40*	.09	.09	.11	.14	.50**	-.10	.42*	-.04	.47**	1.0			
Cu	.16	.18	.27	.26	.43*	.24	.31	.46**	.06	.06	.05	.39*	.04	.19	.39*	.19	1.0		
Cl^{-}	.67**	.54**	.19	.09	.39*	.85**	.16	-.09	-.06	.12	.19	-.04	.15	.79**	.61**	.13	.28	1.0	
pH	.00	.15	.07	.23	.22	-.25*	.32**	.46**	.28*	-.27*	-.37**	.26	-.43*	-.12	-.29	-.36*	.27	-.19	1.0

Table 13. Correlation matrix of major ions and total P in snow core samples collected during March 1978 in northeastern Minnesota. Coefficients are computed from logarithms of concentrations. Asterisks denote significance level

1978 Snow

pH	1.00									
NO_3^-	-.85**	1.00								
$SO_4^=$	-.38*	0.53**	1.00							
NH_4^+	-.03	.19	.60**	1.00						
P_{tot}	-.19	.45**	.52**	.21	1.00					
Cl^-	-.13	.26	.30**	.43**	.05	1.00				
Na^+	-.38*	.51**	.35*	.47**	.15	.57**	1.00			
K^+	-.09	.20	.46**	.58**	.38*	.42**	.68**	1.00		
Ca^{++}	-.12	.34*	.39**	.24	.24	.21	.39*	.39*	1.00	
Mg^{++}	.01	.17	.48**	.32*	.43**	.29	.20	.36*	.41**	1.00
	pH	NO_3^-	$SO_4^=$	NH_4^+	P_{tot}	Cl^-	Na^+	K^+	Ca^{++}	Mg^{++}

Table 14. Correlation matrix of major ions, total phosphorus, and particulates in snow-core samples collected during the winter of 1978-79 along a belt transect from Tewaukon to Hovland. Coefficients were computed from logarithms of concentrations except for alkalinity, which was computed with arithmetic values because of the large number of zero values. Asterisks denote significance level; *$p \leq 0.05$, **$p \leq 0.01$.

	pH	Na^+	K^+	NH_4^+	Ca^{++}	Mg^{++}	Cl^-	NO_3^-	$SO_4^=$	P_{tot}	HCO_3^-	Part.
pH	1.0											
Na^+	.77**	1.0										
K^+	.77**	.81**	1.0									
NH_4^+	-.01	.16	.28*	1.0								
Ca^{++}	.88**	.75**	.69**	.10	1.0							
Mg^{++}	.88**	.75**	.75**	.00	.85**	1.0						
Cl^-	.55**	.79**	.73**	.35*	.53**	.59**	1.0					
NO_3^-	.29*	.29*	.26*	.26*	.53**	.10	.05	1.0				
$SO_4^=$	.60**	.76**	.56**	.29*	.72**	.57**	.66**	.47**	1.0			
P_{tot}	.75**	.67**	.76**	.14	.79**	.69**	.61**	.39*	.62**	1.0		
HCO_3^-	.84**	.63**	.72**	.12	.54**	.71**	.60**	-.08	.37*	.37*	1.0	
Part.	.58**	.49**	.58**	-.16	.53**	.59**	.50**	.14	.35*	.54**	.43**	1.0

Table 15. Equivalent ratios of elements to Aluminum and Iron.

	Tewaukon		Itasca		Hovland	
X	X:Al	X:Fe	X:Al	X:Fe	X:Al	X:Fe
Na^{+}	2.4	7.0	3.2	11.8	6.5	19.8
K^{+}	1.2	3.3	1.2	4.8	1.8	5.4
NH_4^{+}	9.6	25.2	9.3	34.8	16.3	48.1
Ca^{++}	11.2	34.5	14.3	49.4	17.6	51.1
Mg^{++}	3.9	12.1	6.6	24.7	4.6	13.7
Cl^{-}	7.1	20.7	16.9	61.7	22.1	68.7
NO_3^{-}	5.5	15.5	9.4	35.6	17.6	52.6
$SO_4^{=}$	7.4	20.5	11.9	45.1	27.4	81.8
P_{tot}	0.13	0.37	0.14	0.54	0.15	0.47

Table 16. Equivalent ratios of NH_4^+ to $SO_4^=$ for each season and for all data.

Site	Spring	Summer	Fall	Winter	Spring	All Data
Tewaukon	1.40	1.52	1.14	0.55	1.40	1.32
Itasca	1.10	1.29	0.57	0.71	0.92	1.05
Hovland	1.03	0.79	1.29	0.50	1.16	0.94

Table 17. Concentrations of major ions and phosphorus and precipitation depth at selected sites in North America and Scandinavia. All values are volume-weighted mean concentrations over periods of one or more years except the Norwegian values, which are a range of annual volume-weighted means from 6 sites. Concentrations are in $\mu eq\ \ell^{-1}$ except phosphorus which is in $\mu g\ \ell^{-1}$. Superscripts indicate which phosphorus fraction was measured; ^{T} = total P, ^{R} = dissolved reactive P. Precipitation depth is in $\ell\ m^{-2}$
- indicates data not available.

LOCATION	H^+	Na^+	K^+	NH_4^+	Ca^{++}	Mg^{++}	Cl^-	NO_3^-	$SO_4^=$	P	H_2O	TYPE	REFERENCE
Pasadena, CA	87	25	2.1	33	9.6	6.6	29	75	60	-	---	wet only	Liljestrand and Morgan 1978
Muskoka-Haliburton, Ontario	100	16.9	4	31	36	10	9	30	67	24^T	689	wet only	Scheider et al. 1979
ELA, Ontario	10.9	8.3	3.3	20.9	22.5	9.5	9.9	18.5	89.9	40^T	804	bulk	Schindler et al. 1976
Upstate New York	103.3	8.3	3.3	32	57.7	15.8	33.	51.6	113.2	61.7^R	910	bulk	Likens 1972
Hubbard Brook	72.4	5.2	1.8	12.2	8.0	3.3	13.3	23.7	60.3	8^R	1322	bulk	Likens et al. 1977
New York, NY	119	35.8	2.4	11.2	16.1	12.8	43.4	39.1	125.2	-	1303	wet only	Feely and Larsen 1979
Chester, NJ	79.6	17.8	2.0	13.5	6.4	5.1	16.5	33.4	72.7	-	1276	wet only	Feely and Larsen 1979
Coweeta, SC	-	7.4	2.1	1.4	11.5	4.2	20.7	8.6	-	7^R	2130	bulk	Swank and Henderson 1976
Walker Branch, TN	-	10.9	5.1	9.3	51.5	15.8	-	17.9	-	40^R	1530	bulk	Swank and Henderson 1976
Southern Norway	27 55	- -	2 6	11 30	5 14	4 40	5 169	11 32	35 70	-	468 2925	bulk	Wright and Henriksen 1978
Florida	29.5	19.1	5.1	7.1	20.5	10.0	27.6	13.6	42.7	34^T	1215	wet only	Hendry and Brezonik 1980
Iowa	.71	-	-	45.0	-	-	-	42.9	96.9	-	800	bulk	Tabatabai and Laflen 1976
Hovland	21.5	6.1	3.3	37.1	20.0	10.8	26.2	20.7	39.4	28.9	702	wet only	This study
Itasca	10.0	8.7	4.4	33.6	34.5	19.2	46.8	20.0	31.9	14.2	673	wet only	This study
Tewaukon	5.4	11.7	5.9	47.9	52.5	22.5	49.9	25.7	36.3	32.9	405	wet only	This study

Table 18

Average concentration in two groups of dilute lakes and volume weighted average concentration in precipitation at the collector sites nearest these areas. All concentrations in μeq ℓ^{-1} except total phosphorus, which is in μg ℓ^{-1}.

	Dilute Lakes		Precipitation	
	BWCA[1] Minn	Northern[1] Wisc.	Hovland	Itasca
Na^+	40	40	6.1	7.
K^+	22	20	3.	4.
Ca^{++}	155	150	20.	34.5
Mg^{++}	90	70	11.	19.
$SO_4^=$	110	99	39.	32.
$NO_3^- + NH_4^+$	4.6	---	57.8	53.6
P_{tot}	11[3]	15[2]	28.9	14.2
	(n = 5)	(n = 13)		

1. Data from Gorham et al. (in prep).
2. Phosphorus concentration, average of 85 lakes in Northern Wisconsin (sp. cond. ≤ 50 μ S) from Eilers et al. (1979)
3. Phosphorus concentration, average of 3 lakes in BWCA from Tarapchak and Wright (1977).

Fig. 1. Map of Minnesota and surrounding area showing the locations of precipitation collectors and snow-core sampling sites. Rectangle encloses area where snowcores were collected during March 1978.

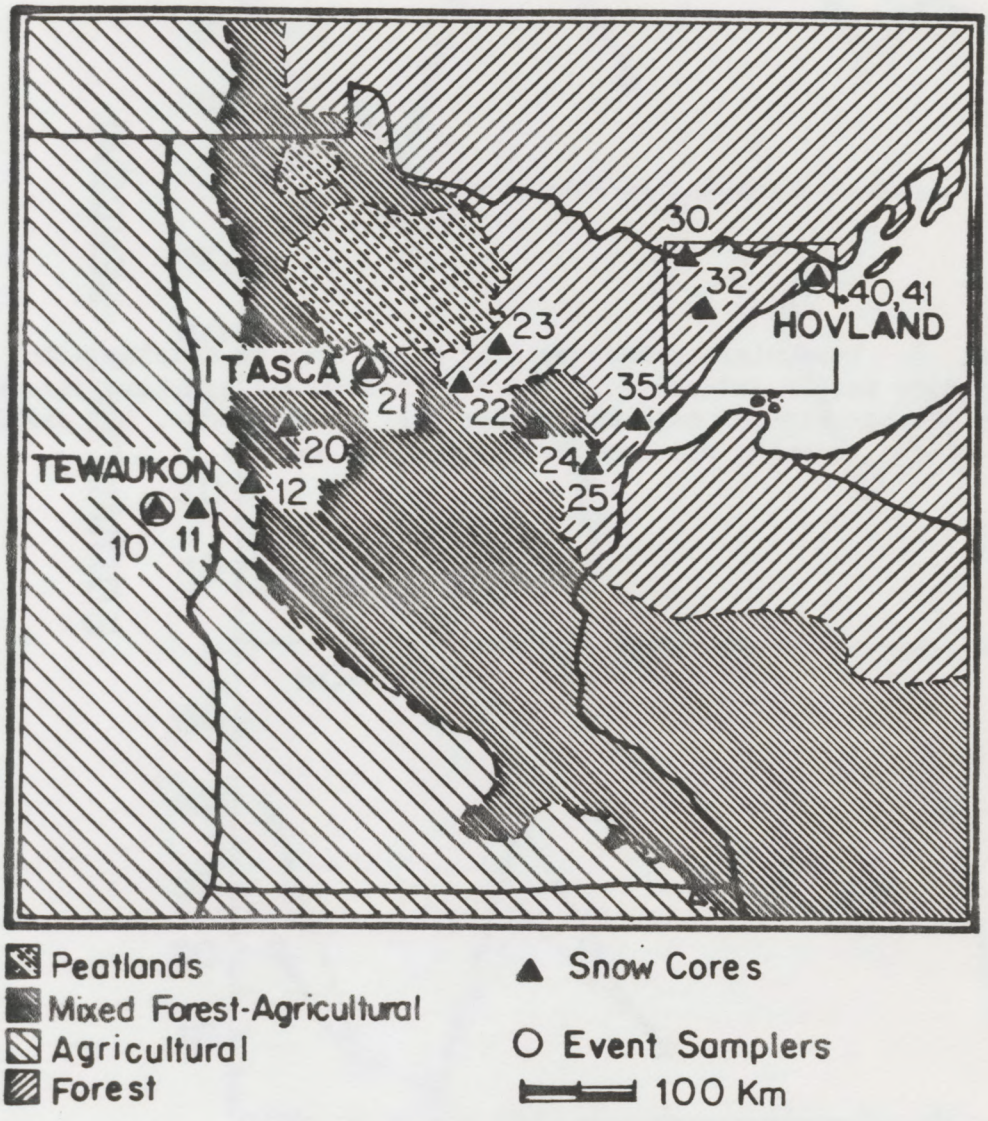

30
32
40,41
HOVLAND
23
ITASCA
21
22
35
20
24
25
TEWAUKON
12
10
11
Peatlands
Mixed Forest-Agricultural
Agricultural
Forest
Snow Cores
Event Samplers
100 Km

Fig. 2. Equivalent percentages of major ions in samples with anion/cation ratios between 0.90 and 1.10 and in all samples, percentages are for volume-weighted mean concentrations. △———△ , All samples ○— — — —○ , Samples with ratios between 0.9 and 1.1

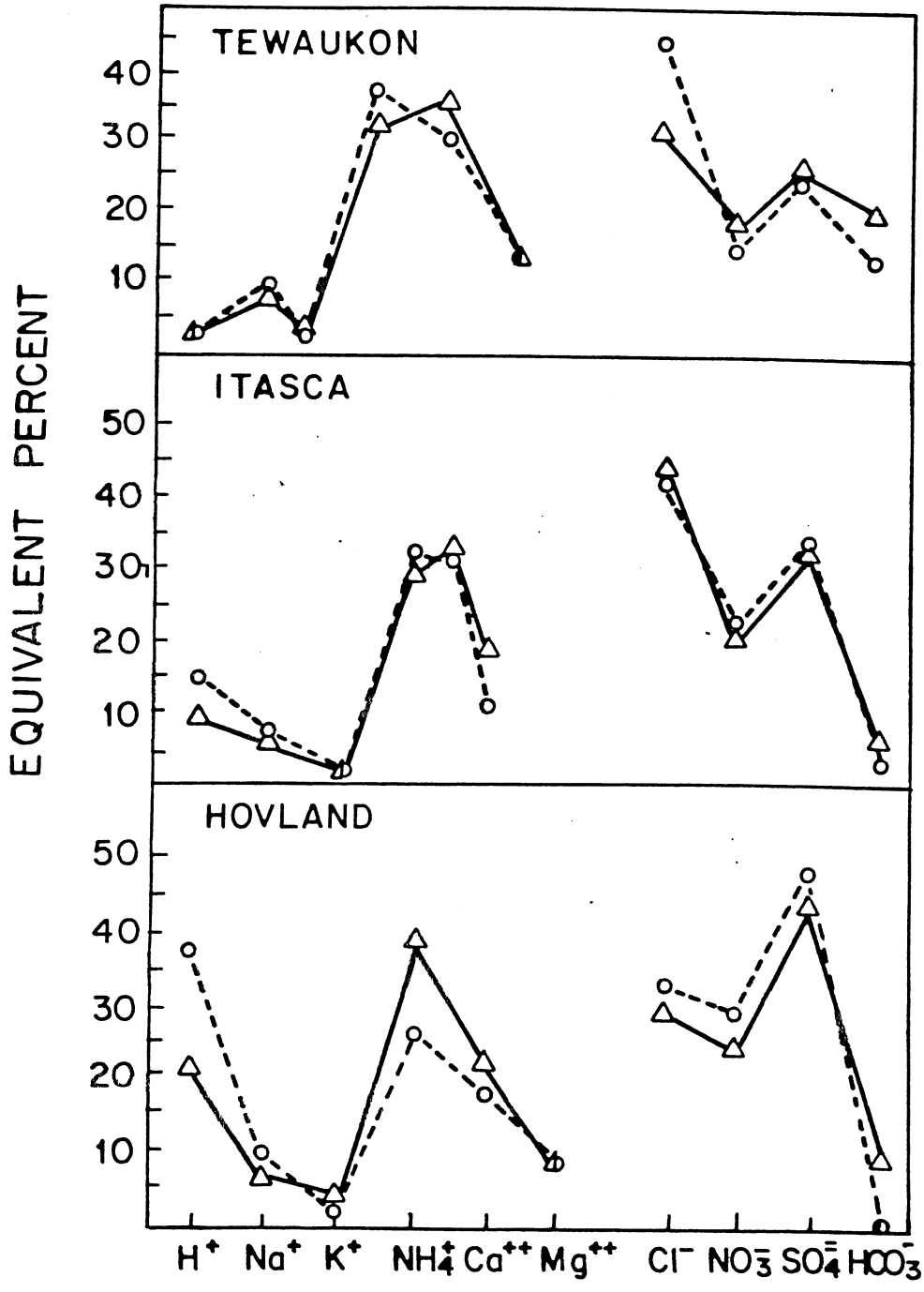

TEWAUKON
ITASCA
HOVLAND
EQUIVALENT PERCENT
40
30
20
10
50
40
30
20
10
50
40
30
20
10
H+ Na+ K+ NH4+ Ca++ Mg++ Cl- NO3- SO4= HCO3-

Fig. 3. pH and sulfate concentrations in snow cores collected during 1979. The location of the sites are indicated in the lower panel.

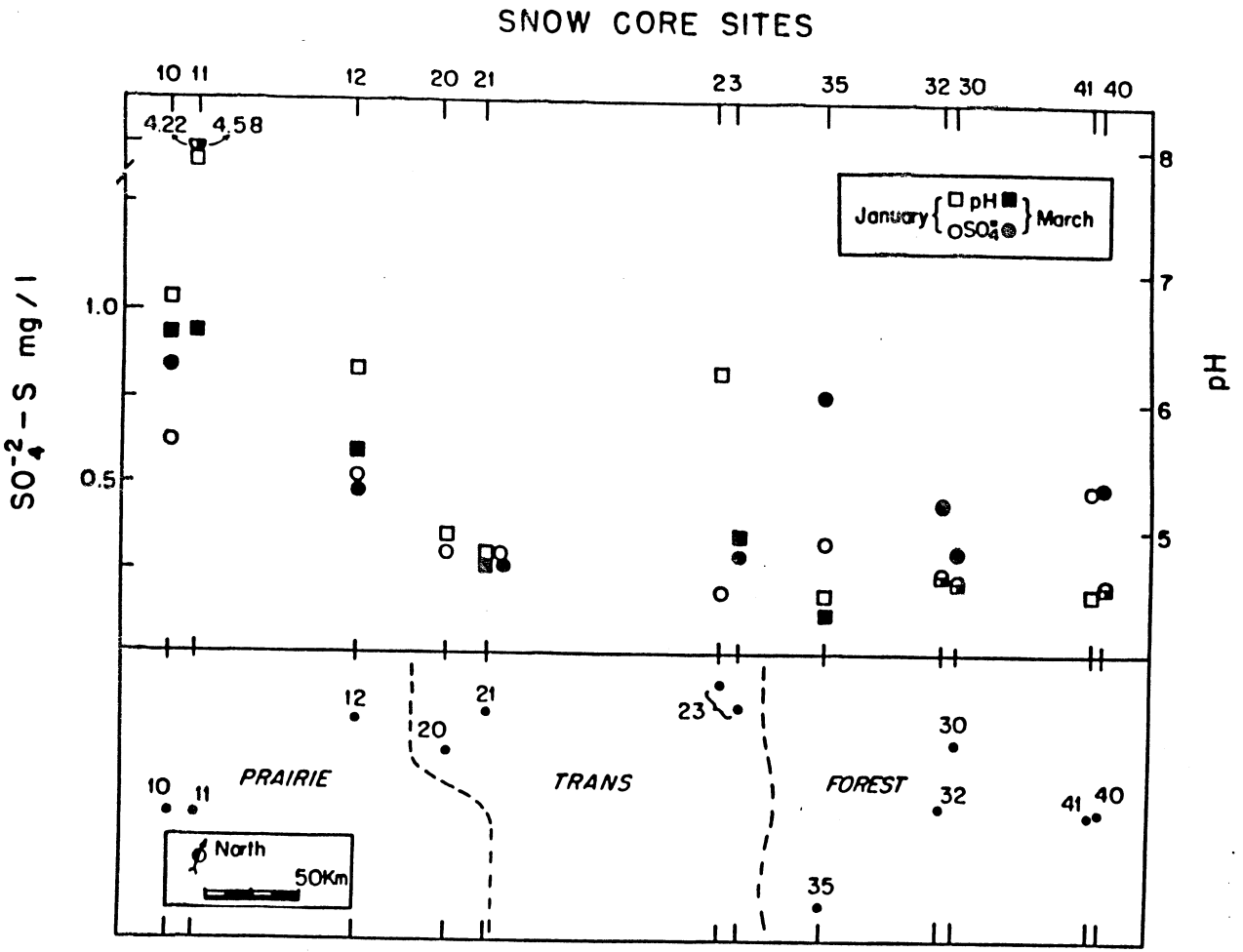

SNOW CORE SITES
10 11
12
20 21
23
35
32 30
41 40
4.22
4.58
January { pH / $SO_4^{=}$ } March
SO_4^{-2}-S mg/l
1.0
0.5
pH
8
7
6
5
PRAIRIE
TRANS
FOREST
North
50Km

Fig. 4. Total P and filterable solids (particles $\geq$ 0.4 µm) in snow cores collected during 1979. The locations of the sites are indicated in the lower panel.

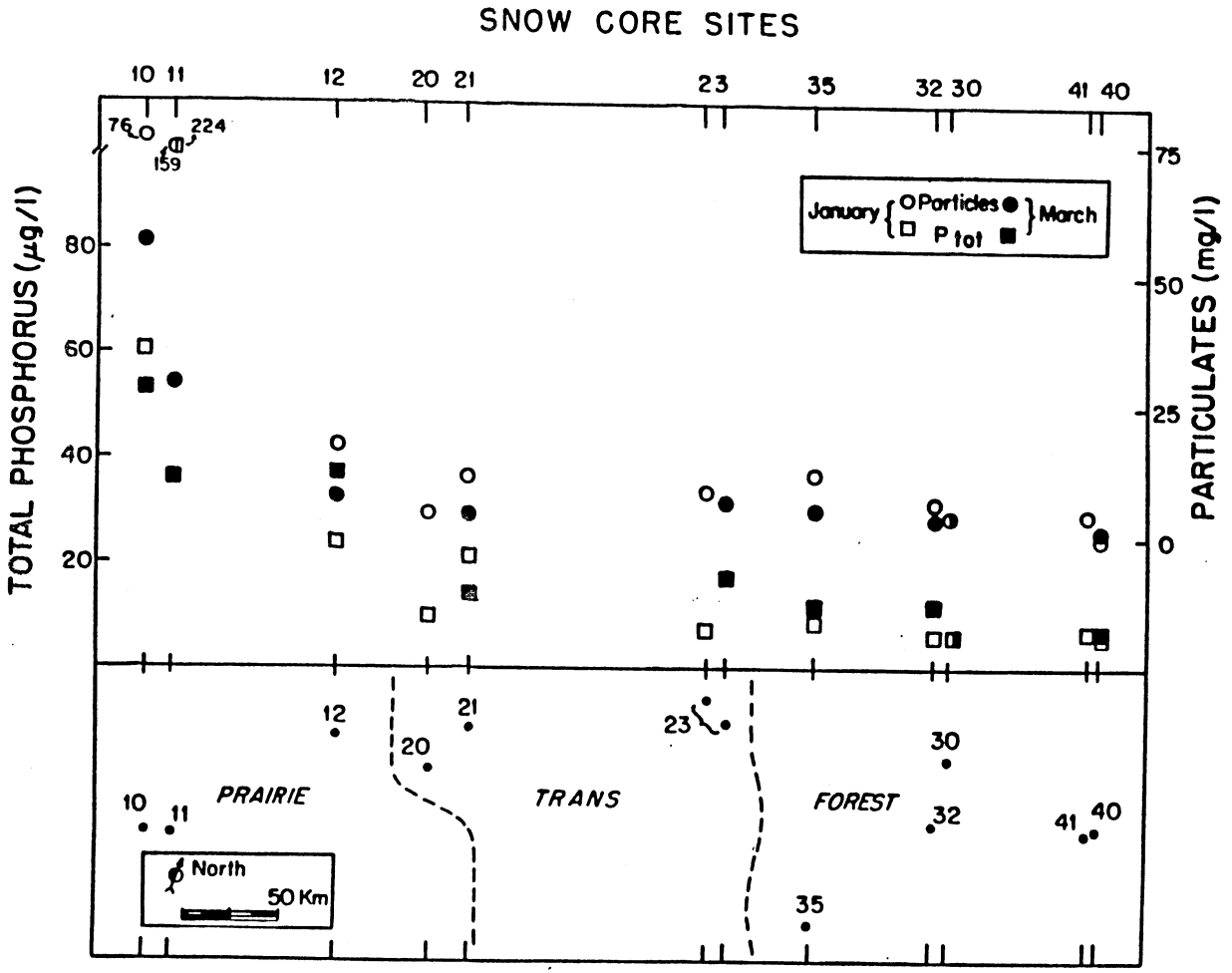

SNOW CORE SITES
10 11
12
20 21
23
35
32 30
41 40
76
224
159
TOTAL PHOSPHORUS (µg/l)
PARTICULATES (mg/l)
80
60
40
20
75
50
25
0
January
Particles
P tot
March
PRAIRIE
TRANS
FOREST
North
50 Km

Fig. 5. pH *vs.* NH_4^+: $SO_4^=$ ratio in samples of precipitation collected at the Hovland site. The regression line and its 95% confidence interval are indicated.

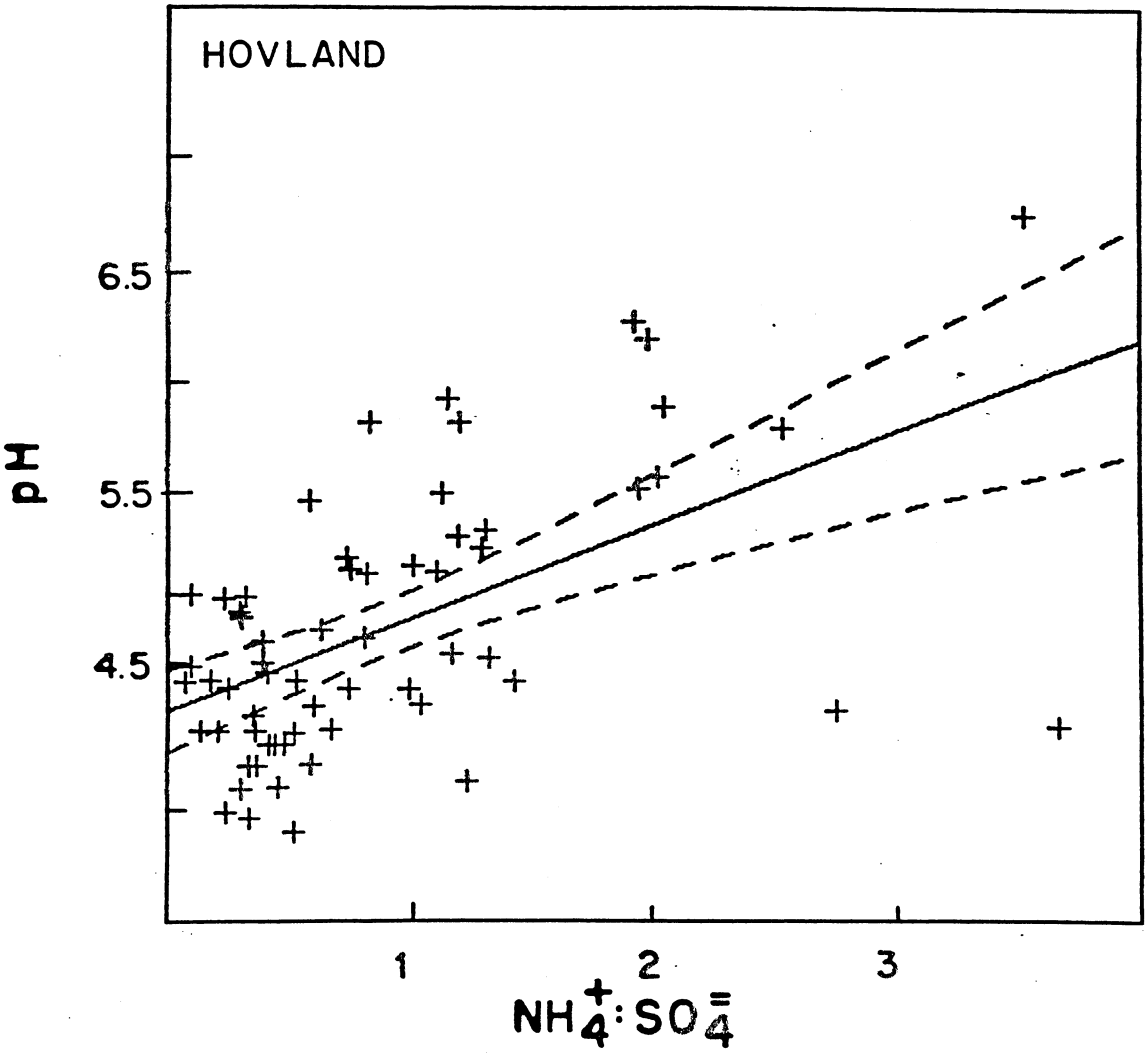

HOVLAND
pH
6.5
5.5
4.5
1
2
3
$NH_4^+ : SO_4^=$

Fig. 6. pH *vs.* NH_4^+ : $SO_4^=$ ratio in samples of precipitation collected at the Itasca site. The regression line and its 95% confidence interval are indicated.

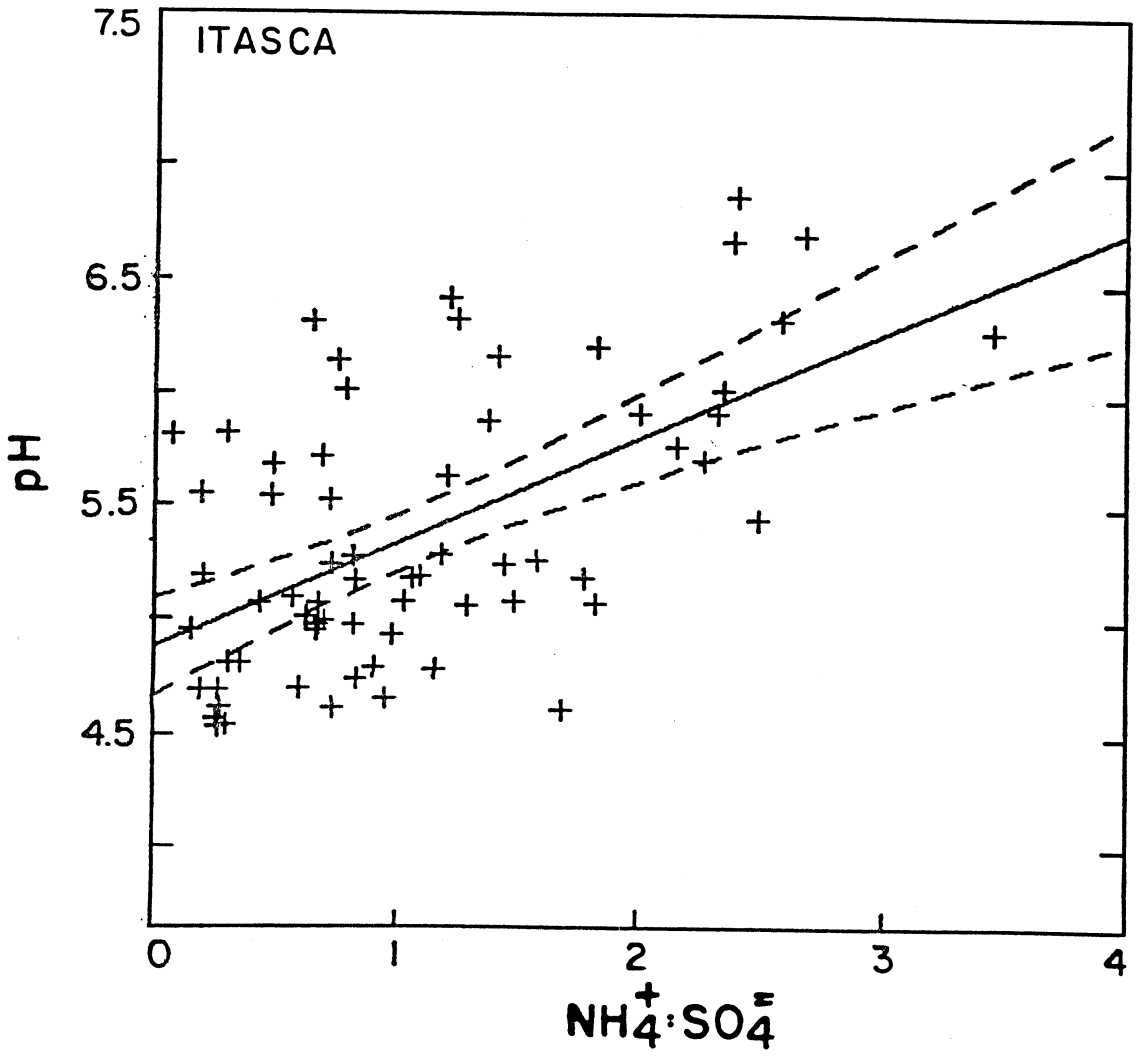

ITASCA
7.5
6.5
5.5
4.5
pH
0
1
2
3
4
$NH_4^+ : SO_4^=$

Fig. 7. pH *vs.* NH_4^+ : $SO_4^=$ ratio in samples of precipitation collected at the Tewaukon site. The regression line and its 95% confidence interval are indicated.

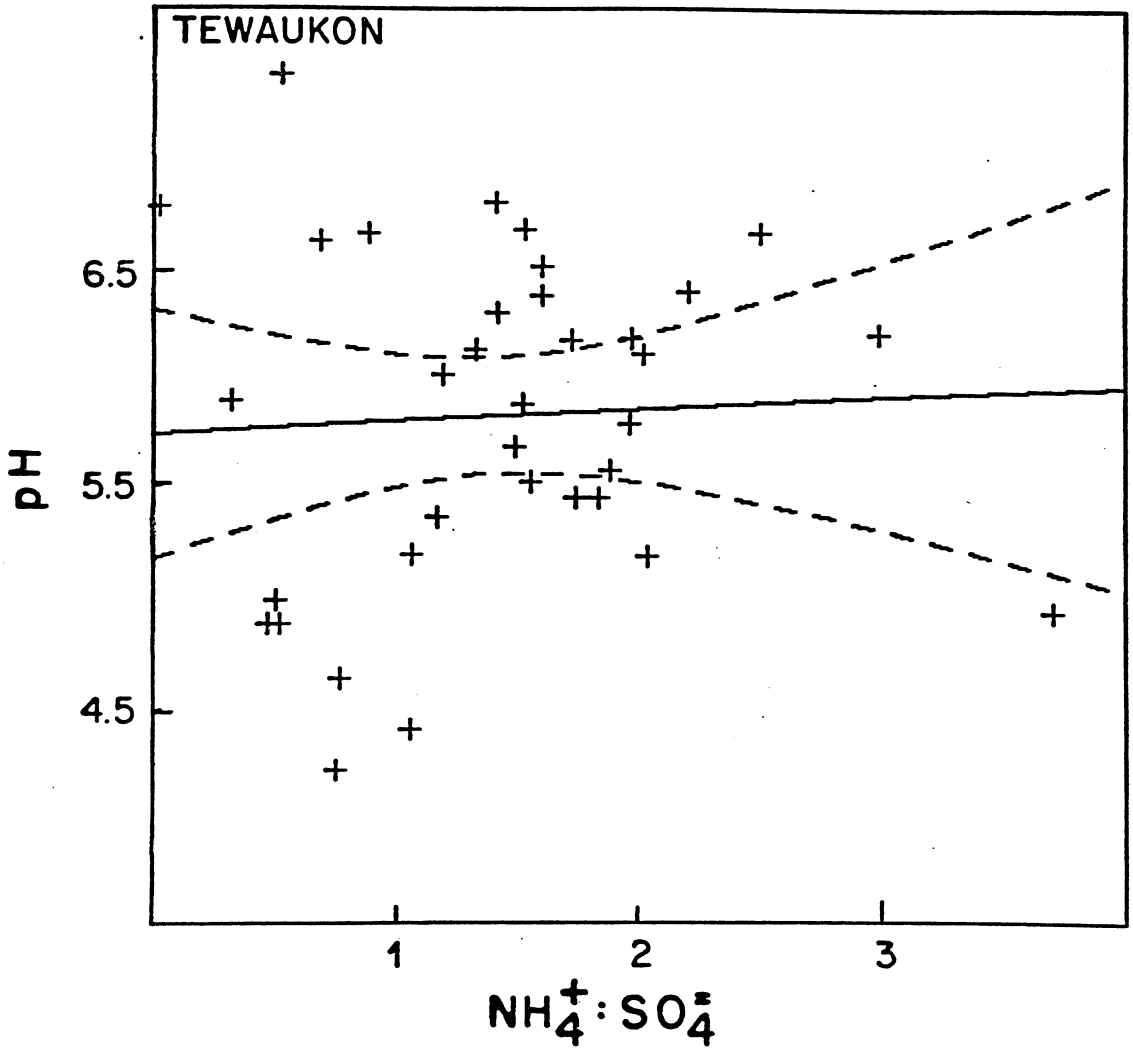

TEWAUKON
pH
6.5
5.5
4.5
1
2
3
$NH_4^+ : SO_4^=$

Fig. 8. pH *vs.* Ca^{++} : $SO_4^{=}$ ratio in snow-core samples collected along a belt transect from Tewaukon to Hovland. The regression line and its 95% confidence interval are indicated.

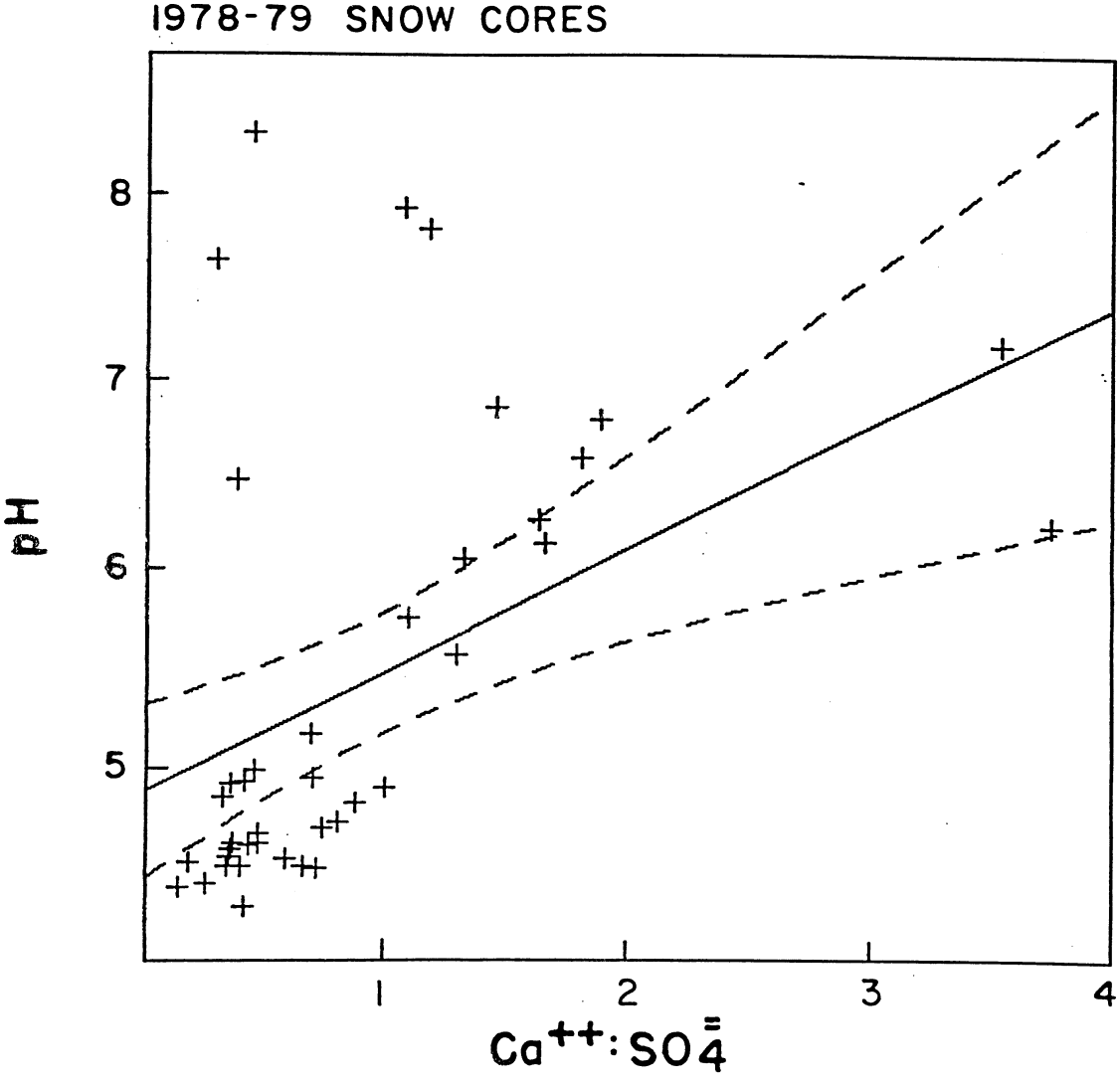

1978-79 SNOW CORES
pH
8
7
6
5
1
2
3
4
Ca++:SO4=

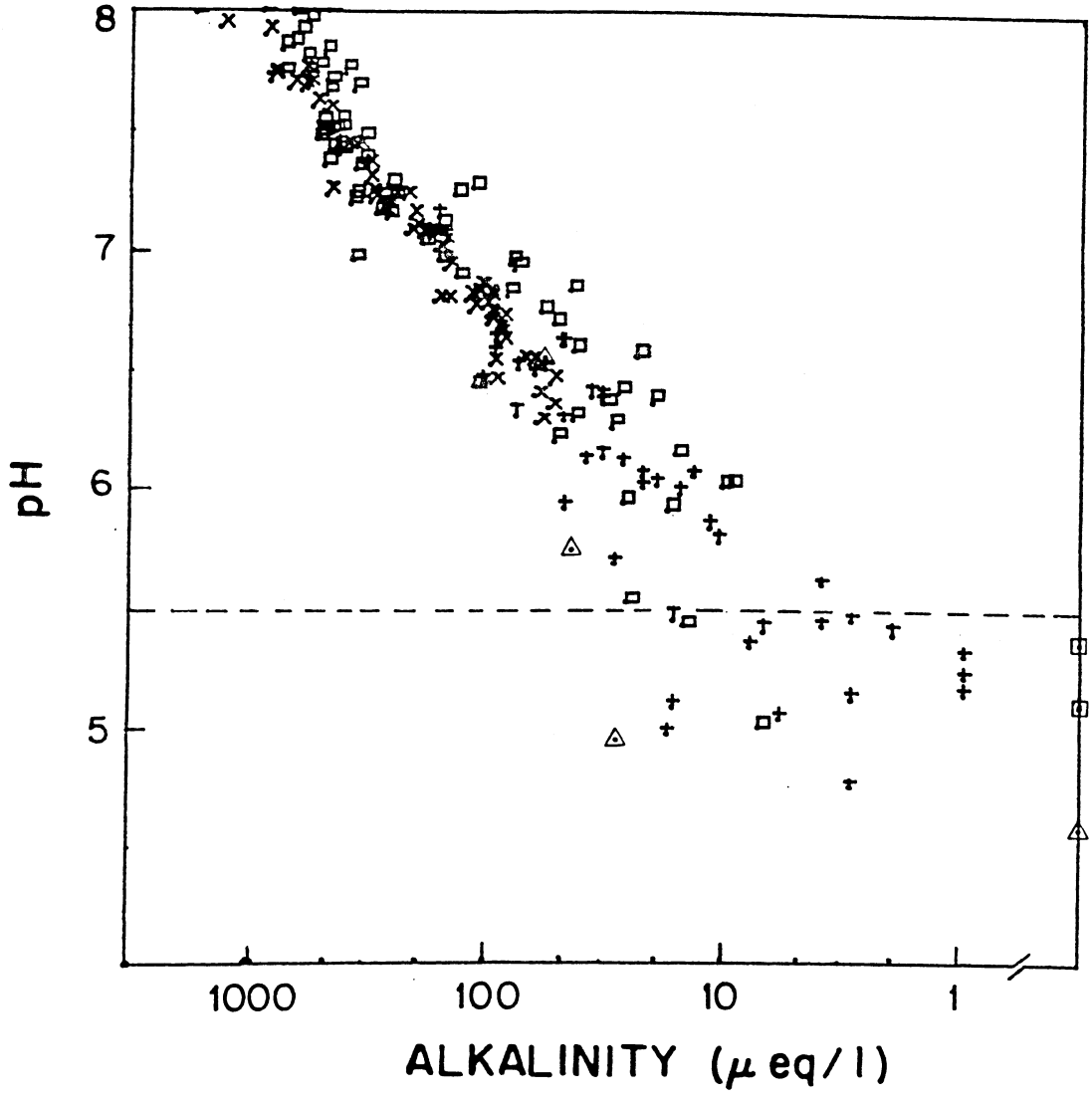
Fig. 9. pH *vs.* alkalinity in lakes in northeastern Minnesota, northern Wisconsin, the Adirondacks, and Southern Norway. Dashed line indicates mean threshold for danger to fisheries.

× Northeastern Minnesota (Glass and Loucks 1980)

□ Northern Wisconsin (Eilers *et al.* 1979)

\+ Adirondacks (Schifield 1976)

△ Southern Norway (Wright and Henricksen 1978)


8
7
6
5
pH
1000
100
10
1
ALKALINITY (μ eq/l)

Appendix 1

COLLECTOR SITE DESCRIPTIONS

Tewaukon Site

The Tewaukon Wildlife Refuge is located at 46° N - 97°22' W. The nearest major population center is Fargo-Moorhead, ND-MN, 110 km to the NE, which has a population of 88,000. The refuge encompasses numerous lakes, ponds, and marshes; the uplands are vegetated predominantly by grasses with a few small woodlots. Intensively cultivated agricultural land surrounds the refuge. The collector was situated 25 m north of a dirt parking area at the refuge headquarters, and 150 m east of a band of small trees on the near side of a lightly used asphalt road. Marshes and Lake Tewaukon bordered the collector on the north and east. At least 1.5 km separated the collector from the cultivated areas to the north and south, and 6.5 km to the east and west.

Itasca Site

The Lake Itasca Biological Station in Itasca State Park is located at 47° 15' N - 95° 10' W. The nearest population center is Bemidji, MN, 36 km NNE of the site, which has a population of 12,000. The Biological Station is on the east shore of Lake Itasca, and is surrounded by mixed coniferous-hardwood and coniferous forests on the remaining sides.

The collector was in the center of a small meadow at the Station. A very lightly used dirt service road approached the meadow along the south side; all other roads and parking areas on the Station were paved.

Hovland Site

The Hovland site was in a remote forested area at 47° 50' N - 90° W. The nearest urban-industrial area is Thunder Bay, Ontario, 90 km to the NE, which has a population of 108,000 and is a paper-mill center. Paper-mill odors are occasionally noticeable at Hovland. The aspen and spruce-fir forests in the Hovland area are managed for logging and a site within 1 km of the collector was cut during the study period.

The collector site was in a large field adjacent to a permanent dwelling. The house, which was heated by a wood stove, was 100 m west of the collector, and predominant winds blew from the collector toward the house. A line of trees shielded the collector from a gravel road 250 m north of it.

The site was 2 km inland from Lake Superior and 120 m above the lake level. Precipitation depth along the north shore of Lake Superior is variable; there were occasionally significant differences between precipitation collected in the rain gauge at the Department of Natural Resources district office, which was near the lake shore, and the precipitation in the collection bucket at the site. All calculations using precipitation volume are based on precipitation collected in the samplers.

Snow-Coring Sites

1978 Samples

I collected snow pack samples at 8 sites shown in Fig. I-1 in Lake and Cook Counties of northeastern Minnesota on 17-19 March 1978 that were far from local sources of contamination. Table I-1 describes some features of the sites and the conditions at the time of sampling. Several sites could only be reached by ski or snowshoe, and the Forest Service roads

along which half the sites were located were snow-covered enough to discourage travel.

1979 Samples

During the fall of 1978 I set out polyethylene sheets on the ground at the three event-collector sites and at two additional sites in northeastern Minnesota. The plastic sheet at Tewaukon was located in an opening within a small woodlot behind the refuge headquarters building south of the event-collector. The trees around the sheet protected it from the wind and allowed better retention of snow. I also collected snow cores in the marshy area around the margin of Lake Tewaukon. The plastic sheets at Itasca and Hovland were adjacent to the event collectors. At Moose Lake, site 30, the plastic sheet was set out in a small clearing in an aspen forest. The Isabella site, no. 32, was in a large field upwind of the Environmental Learning Center, an outdoor education facility operating during the winter.

Snow samples were collected on several occasions during the winter of 1978-79 at sites across the region; the location, sampling dates, and weather conditions for each site are listed in Table I-2. Samples collected during 18-20 November 1978 along a transect from a point 65 km west of Duluth, MN, to Tewaukon, ND, included snow that fell during the previous week and snow falling in a storm on 18 November. In late December I sampled snow at French River and Moose Lake.

Sites along the entire transect from Tewaukon to Hovland were sampled in January and again in March. Snow fell immediately before and during the 19-22 January coring expedition. Temperatures rose above $0^{o}C$ and light rain fell across the region just before and during the 17-19 March snow-

coring expedition. The snow was melting rapidly at the sites in northeastern Minnesota by the time I got to them. I sampled the snow pack at Hovland again on 22 March after additional melting and rain. The French River site was sampled a second time on 4 March shortly after a 20-cm snowfall. I collected both a vertical core and a sample of the fresh snow; data from the vertical core are used in Figs. 3 and 4.

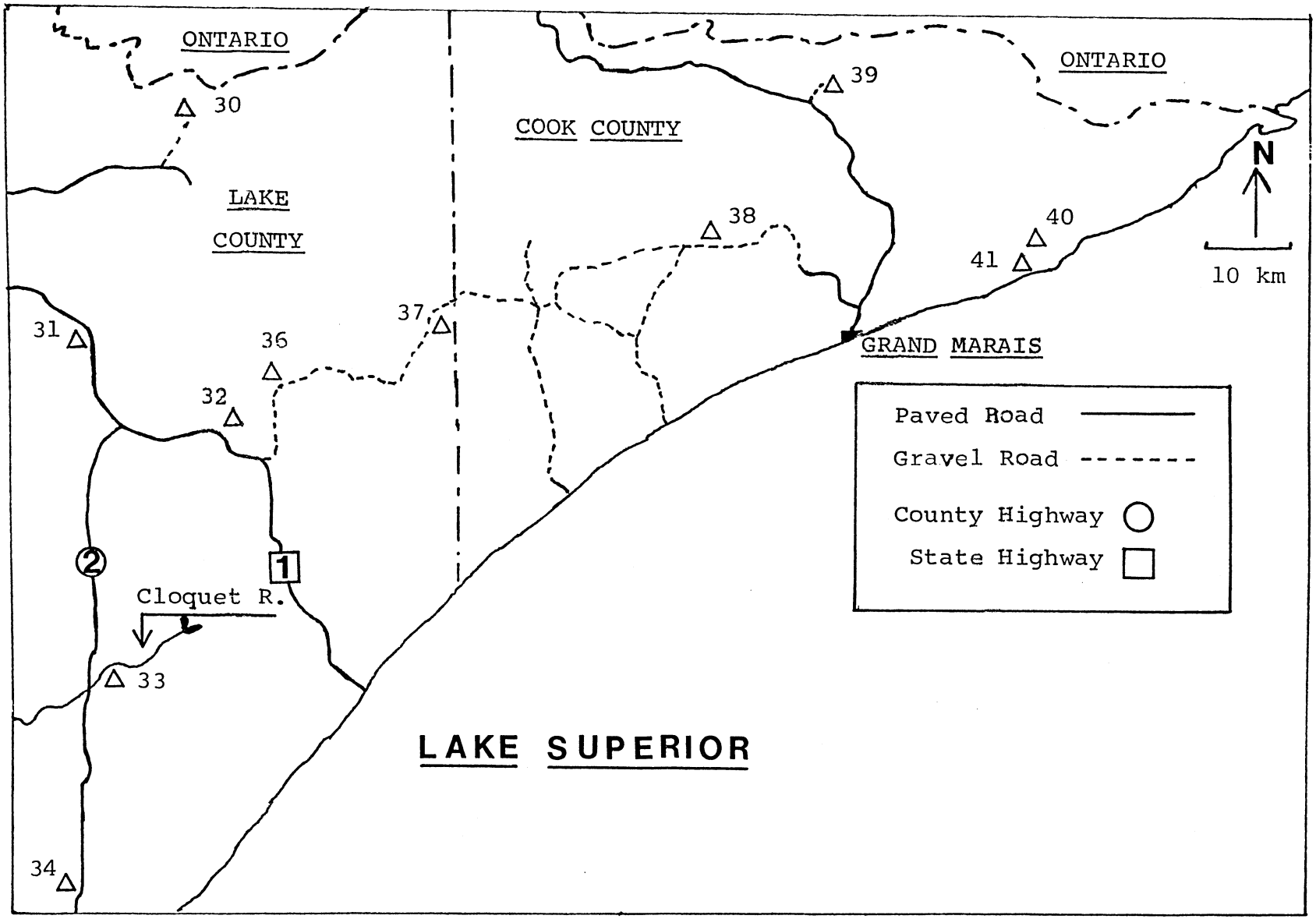
Table I-1 Description of snow-core collection sites in Northeastern Minnesota during March 1978.

Site	Access	Description of Surroundings	Weather Conditions and Remarks	Date
34	Ten km N of Two Harbors, MN, Unplowed road off Lake Co. Highway 2	Old field, 100 m west of highway	Clear weather Vertical core over grass	3/17
33	Cloquet River, Snowshoed E of Lake Co. Highway 2	River bank surrounded by forest	Clear weather Vertical core over ice.	3/17
31	Snowshoed through reseeded clearcut alongside Minn. Highway 1	Surrounded by shrubs and scattered aspens	Clear weather Vertical core over vegetation	3/17
32	Cross-Country ski trail far from nearest road, near Isabella, MN	Small grassy clearing in forest	Clear weather Vertical core over grasses	3/17
36	Short stretch of unplowed road off Forest Service road	Road clearing surrounded by forest	Snowing at time Vertical core over grasses	3/18
37	Unplowed trail off Forest Service road	Roadway clearing surrounded by forest	Snowing at time Vertical core over vegetation	3/18
38	Alongside Forest Service road	Roadway clearing surrounded by forest	Snowing at time Vertical core over vegetation	3/18
39	Unplowed road to Forest Service campground	Roadway clearing surrounded by forest	Weather clearing, snowed day before Vertical core over road surface	3/19

Table I-2 1978-79 snow core sites, descriptions, sampling times, and weather conditions. 10-12 are Prairie sites, 20-25 are transition sites, 30-41 are northeast forest sites.

Site	Description	Weather Conditions date early winter	mid-winter	late winter
10	Plastic sheet site in woodlot at Tewaukon	Cloudy weather following snow-storm, 11/20	Snowing at time 1/19	Cloudy and warm Beginning to melt in open areas, snow wet but not saturated, 3/17
	Marshy margins of Lake Tewaukon	Same	Same.	Same
11	East shore of Elsie Lake, S. of Hankinson ND	Not sampled	Sampled shortly after end of snow-storm, 1/19	Cloudy and warm, Snow wet but not saturated, 3/17
12	Unplowed parking area at Buffalo R. State Park surrounded by river-bottom forest	Not sampled	Snowing at time, 1/19	Cloudy and warm, snow wet but not saturated, 3/17
20	Wet meadow-fen surrounding a lake in the Smokey Hills State Forest	Not sampled	Snowing at time, 1/19	Snow wet, stained yellow by seepage from soil solution 3/17
21	Plastic sheet near event-collector at Itasca	Sampled shortly after end of snow snowstorm, 11/19	Snowing at time, began previous day, 1/20	Misty rain beginning, 2nd day of melt, snow slushy next to plastic 3/18
	On Lake Itasca ice	Same	Same	Not sampled
22	Unplowed road in campground	Sampled shortly after end of snow storm, 11/18	Not sampled	Not sampled
23	On ice of tributary to Bigfork R. surrounded by ash trees	Not sampled	Snowing at time, 1/20	River open, not sampled
23b	Thistledew Lake, on ice	Not sampled	Not sampled	Raining at time, Snow wet and slushy, 3/18
24	Grassy clearings on bluff over Prairie R.	Snowing at time, 11/18	Not sampled	Not sampled
25	Power-line clearing at edge of woods in Savanna State Forest	Snowing at time, 11/18	Not sampled	Not sampled

Fig. I-1. Locations of March 1978 snow-core sampling sites. Sites 30,40,and 41, which were only sampled in 1978-79, are also included.


ONTARIO
30
LAKE
COUNTY
COOK COUNTY
39
ONTARIO
N
10 km
38
40
41
37
31
36
GRAND MARAIS
32
Paved Road
Gravel Road
County Highway
State Highway
2
1
Cloquet R.
33
LAKE SUPERIOR
34

Appendix 2

Collectors

The automatic wet-dry precipitation collector (Aerochem-Metrics model 201), which is pictured in Fig. II-1, has two containers. Each has a 642-cm^2 opening 1.2 m above ground level. The collector legs and frame are constructed of anodized aluminum. The movable roof is of polycarbonate and the seal is a polyurethane pad enclosed in polyethylene. The buckets are made of high-density polyethylene.

The dry-collection bucket is open when there is no precipitation. A sensor, which detects a resistance change when moisture collects on its surface, activates a motor that moves the cover off the wet-collection bucket and onto the dry-collection bucket. A spring provides a positive seal when the cover is over either bucket. A heating element within the sensor warms the surface to evaporate moisture after precipitation ceases; the motor is then activated to move the cover back to its original position. During cold weather the sensor surface is heated to melt snow as it falls.

The collectors operate on either 110 V AC or 12 V DC current. They were first installed using 12 V DC batteries at all the sites, but these batteries failed during cold weather. The collectors at Itasca and Tewaukon were converted to 110 V AC current, but since this was impractical at Hovland the collector operated as a bulk collector during early winter 1979 until a new heavy-duty battery arrived.

Bucket Cleaning

Before being sent to the field the buckets were thoroughly cleaned.

I scrubbed them with hot soapy water, and after rinsing with hot tap water, filled them with 25% HCl to ensure removal of any trace-metal contamination. After soaking for at least one hour in the acid, the buckets were rinsed repeatedly with glass-distilled, deionized H_2O (Corning Megapure), until a portion of rinse water left to stand in them had specific conductivity < 2 μS. When the conductivity measurement indicated that all traces of acid were rinsed away, I covered the bottoms of the buckets with fresh Megapure water and shipped them to the collector sites. Polyethylene bottles used for storing the samples (or shipping those of small volume) were washed and rinsed in the same manner.

Fig. II-1. The precipitation collector at the Tewaukon site. Note the prongs of the bird-off.

Appendix 3

LABORATORY PROCEDURES

Sample Handling

Figure III-1 indicates the scheme followed when the samples arrived at the laboratory. They usually arrived in mid-morning and I began working on them immediately. In cases where the volume was insufficient for complete analysis, procedures nearer the top of the figure had priority over procedures below them. I added 250 ml of Megapure water to dry-collection buckets. After scraping them with a polyethylene scraper to dislodge material on the walls, they were handled by the same procedures as the wet-precipitation samples. After weighing and melting, snow samples were analyzed by the same procedures as wet-precipitation samples, except that the remainder of the sample was kept in the bag rather than being poured into a new container for storage.

Analytical Methods

I measured pH with a Radiometer TTT1C pH meter-autotitrator equipped with a glass electrode and KCl/porous-pin reference electrode. Conductivity was measured with an Industrial Instruments RC16B2 conductivity bridge with a platinized conductivity cell. The cell constant was checked periodically against a standard KCl solution. The metal cations Na^{+}, K^{+}, Ca^{++}, and Mg^{++} were determined by Atomic Absorption Spectrophotometry (AAS) with a Varian AA175. A standard curve based on a series of standards prepared from concentrated stock solutions was made before each series of analyses. Correlation coefficients for the standard-curve regressions exceeded 0.99. The instrument settings used in the analyses were as

recommended by the manufacturer. I added La^{+3} to aliquots of sample to prevent interference in the Ca^{++} and Mg^{++} determinations. A La^{+3} concentration of 0.05% gave satisfactory results. To account for interference with K^{+} determinations, I spiked the K^{+} standards with a Na^{+} concentration equal to the mean Na^{+} concentration in the samples. Samples with Na^{+} concentrations higher than average were analyzed separately and compared to K^{+} standards made with more concentrated Na^{+} spikes.

The anions Cl^{-}, NO_3^{-}, and $SO_4^{=}$ were determined with a Dionex model 10 Ion Chromatograph (IC) connected to a strip chart recorder. The standard eluent, 3.2 mM $NaHCO_3$ + 2.4 mM Na_2CO_3, was used at a flow rate of 184 ml/minute. Separatory column length totalled 650 mm, and the sample injection loop was 500 µl. Samples were spiked with eluent solution to eliminate the conductivity dip. Concentrations were determined from a standard curve based on peak height. Correlation coefficients for the NO_3^{-} and $SO_4^{=}$ standard-curve regressions were $\geq$ 0.99. Because Cl^{-} eluted at the same time as the dip caused by the less conductive sample solution, its analytical results were not as good as those for NO_3^{-} and $SO_4^{=}$.

I used a phosphorous method based on the technique of Murphy and Riley (1962) as modified by Eisenreich et al. (1975). In addition I removed turbidity by filtering the sample through Whatman GFA filters after development of the blue color. The absorbance of filtered samples and standards was measured in 10 cm cells at 882 nm, using a Beckman DU spectrophotometer. The concentration of NH_4^{+} was determined by the phenol-hypochlorite method (Solórzano 1967,

Stainton et al. 1977) in unfiltered samples that had been kept refrigerated. The absorbance of samples and standards was read in 1 cm cells at 640 nm with a Beckman DU spectrophotometer.

Alkalinity was determined by Gran Titration (Dryssen and Sillén 1967, Stumm and Morgan 1970). A 50-ml aliquot of sample was bubbled with air passed over Ascarite™ to remove CO_2. The sample was repeatedly titrated to pH 5.5 with .01 N acid and purged of CO_2 until a constant pH of $\tilde{}$ 5.5 was obtained. I noted the volume of acid used to that point, and continued adding it in small increments. The pH was recorded after each addition down to pH < 4.5. The F value, computed by

$$F = 10^4 (V_o + V_a) 10^{-pH}$$

where V_o = initial volume of sample (50ml) and V_a = volume of acid added up to that point, was plotted against volume of acid added (V_a). The equivalence point was calculated from the x-intercept of the straight line portion of the F vs. V_a plot. Alkalinity was calculated from the volume of acid at the equivalence point, the concentration of titrant, and the initial volume of sample.

Appendix 4

ANALYTICAL QUALITY CONTROL

Precision and Accuracy

I calculated coefficients of variation (precision) and relative error (accuracy) according to Standard Methods (APHA 1976) using the concentrations, responses (peak height or absorbance), and concentrations predicted from the regression equations for all standard curves run during the study period. The coefficient of variation is the standard deviation of the predicted standard concentration expressed as a percentage of the mean predicted concentration for all standards at that concentration. The relative error is the deviation between the true concentration and the predicted concentration expressed as a percentage of the true concentration. The estimates of precision and accuracy for the major ions and P at low and moderate concentrations are presented in Table IV-1.

Detection Limits

Detection limits for the cations determined by AAS were estimated from the results of a series of replicate determinations of two standards at low concentration following a method described by Slavin et al. (1972). Theoretically the detection limit estimated by this method is the concentration at which the absorbance is equal to twice the standard deviation of repeated measurements of that concentration. For the anions I set the detection limit at the concentration of a peak with height twice the fluctuation in the baseline. For NH_4^+ I used the concentration at an absorbance twice the standard deviation of the blank absorbances. The absorbance of a P standard at 1 μg l^{-1} was in all

cases greater than or equal to the blank absorbance; I used this value as the detection limit for P_{tot} determinations. Table IV-1 presents the estimated detection limits for major ions and P_{tot}.

Blanks

In general blanks for the buckets and sample containers were at or near the detection limits for all ions except Cl^-. However, a few blanks did have elevated concentrations of Na^+, K^+, Ca^+, and Mg^{++}. The concentrations of NH_4^+, NO_3^-, and $SO_4^=$ in all blanks were at or below the detection limits. An additional series of 5 blanks that were kept in sample containers and analyzed along with a series of synthetic standards had undetectable concentrations of all ions except Cl^-. Because none of the blanks were consistently above detection limits, I chose to ignore blank corrections. Occasional contamination may have occurred in the samples, but this should be a random source of error; a correction based on the mean concentration in all the blanks would not be valid for the majority of the samples. The possibility of occasional contamination will not affect the conclusions drawn from comparisons of concentrations at the three sites, but it may be a factor in the lack of good ionic balances for some samples if contamination was not equal in all aliquots used in analyses.

Analyses of Synthetic Standards

Analytical results are presented in Table IV-2 for a set of standards made from serial dilutions of three replicate synthetic-standard solutions. They show good agreement among the replicates and a linear response to dilution, especially in the lower concentration range. Fig. IV-1, a plot of cations vs. anions, shows that the ionic

balances were excellent for this set of standards. The conductivity calculated from equivalent conductances and measured concentrations is in excellent agreement with the measured conductivity (See Fig. IV-2).

On two occasions about 400 ml of a synthetic-standard solution was placed in a clean collection bucket and allowed to stand at room temperature for several days. A separate aliquot of the standard was stored in a polyethylene sample bottle in the refrigerator. After its removal from the bucket the standard was stored in a similar bottle. The normal synthetic standards and those stored in collection-buckets were analyzed shortly after the latter were removed from the bucket and again at a much later date. The results are presented in Table IV-3.

These results suggest that contamination was a problem for some ions, but the concentrations of NO_3^- and $SO_4^=$ did not undergo significant changes either in the buckets or during extended storage. Even after extended storage the concentrations of NH_4^+ did not change appreciably. The ionic balances for this set of analyses were also quite good. Because of the apparent contamination problem I reduced the concentration of HCl used to clean the buckets from 50 to 25%, rinsed the buckets even more thoroughly than before, and allowed the rinse water to stand in the buckets overnight before checking its conductivity. The contamination suggested by these tests does not seem to be as great a problem in the samples. The concentrations of ions in precipitation samples are comparable to the concentrations apparently being leached in the bucket tests; if the samples were contaminated to the same degree then the actual concentration in precipitation would have been negligible, which is highly unlikely. For comparisons of precipitation at the three sites, possible contamination does not affect the results.

Furthermore, I stress that no evidence of NO_3^- of $SO_4^=$ contamination was found.

Phosphorus appeared to decrease in the synthetic standard tests, but no such low concentrations were ovserved in the samples themselves. I suspect that in the synthetic standard the PO_4^{-3} standard was being adsorbed by the bucket walls. In the samples P was present in particulate and/or other forms besides ortho-P, and any PO_4^{-3} present in the sample could also be adsorbed by the particulates in the sample so as not to be lost from solution. Measurements of dissolved P in a selection of samples indicated that P was predominantly in a $\geq$ 0.4 fraction.

Appendix 5

Ionic Balances

Table V-1 presents the mean ratio of anions to cations, $\Sigma-/\Sigma+$; the means are all between 0.95 and 1.05. The distribution of ion balances for dilute lake-water samples is comparable to the distribution for the event-precipitation samples. The 1978-79 snow samples had the best ion balances. Figs. V-1a-e, plots of ion ratios *vs.* conductivity, indicate that the most diulte samples had the poorest ion balances. The spread of ion balances, however, is greater in the Tewaukon and Itasca samples than in those at Hovland. The higher concentrations of particulates in Tewaukon and Itasca samples compared to snow samples or Hovland precipitation samples, may be a factor in this. Alternatively, because one ion, H^+, makes up a greater share of the ions in the snow-core and Hovland precipitation samples, their ion balances may be better.

Table IV-1. Precision, accuracy, and detection limits for analyses of major ions and P_{tot}. Precision and accuracy are expressed in percent; detection limits are in mg ℓ^{-1} except for P_{tot}, which is in $\mu g\ \ell^{-1}$.

	Estimated at 0.05 mg $^{-1}$		Estimated at 0.5 mg $^{-1}$		
	Precision	Accuracy	Precision	Accuracy	D.L.
Na^+	10	4.5	9	2.3	0.01
K^+	25	1.2	4	0.1	0.005
NH_4^+	16	10	4	1.0	0.02
Ca^{++}	20	1.1	3	0.2	0.015
Mg^{++}	10	4	2	0.4	0.002
Cl^-	--	--	--	--	--
NO_3^-	13	0.1	3.2	0.2	0.01
$SO_4^=$	16	11	3.4	0.3	0.01
	Estimated at 4 $\mu g \ell^{-1}$		Estimated 100 $\mu g \ell^{-1}$		
P_{tot}	18	5.3	3.4	0.68	1

Table IV-2. Analytical results for synthetic precipitation standards. A,B, and C are replicate standards, numbers preceeding the letters indicate the concentration factor, and subscripts indicate replicate dilutions. Conductivity in μS and remaining ions in mg ℓ^{-1}.

	pH	Cond	Na^+	K^+	NH_4^+-N	Ca^{++}	Mg^{++}	Cl^-	NO_3^--N	$SO_4^=$-S
5XA	4.11	117.0	1.19	1.91	2.11	1.95	3.47	4.66	2.10	7.03
$5XA_2$	4.11	117.9	1.16	1.89	2.12	1.94	3.46	4.75	2.08	6.82
5XB	4.10	121.3	1.19	1.92	2.10	2.17	3.48	5.32	2.14	6.82
5XC	4.10	119.5	1.18	1.88	2.15	1.96	3.45	4.51	2.07	6.88
2.5XA	4.40	61.2	0.61	0.99	1.09	0.99	1.74	2.55	1.03	3.42
2.5XB	4.40	60.3	0.59	0.99	0.91	1.09	1.77	2.65	1.08	3.42
2.5XC	4.39	61.9	0.58	0.99	1.06	0.99	1.76	2.65	1.06	3.53
1XA	4.81	22.4	0.33	0.41	0.41	0.41	0.71	1.19	0.41	1.34
$1XA_2$	4.80	24.7	0.23	0.40	0.43	0.40	0.70	1.23	0.44	1.44
1XB	4.78	25.3	0.25	0.41	0.41	0.45	0.73	1.05	0.42	1.44
$1XB_2$	4.78	25.7	0.24	0.41	0.37	0.46	0.73	1.10	0.44	1.44
1XC	4.79	25.7	0.24	0.40	0.44	0.41	0.72	1.08	0.42	1.30
.5XA	5.07	13.1	0.25	0.19	0.19	0.27	0.38	0.50	0.21	0.69
$.5XA_2$	5.02	13.2	0.12	0.20	0.20	0.27	0.38	0.52	0.21	0.74
.5XB	5.03	13.3	0.13	0.20	0.20	0.26	0.38	0.51	0.20	0.70
$.5XB_2$	5.01	14.0	0.12	0.20	0.20	0.23	0.39	0.65	0.21	0.73
.5XC	5.06	13.2	0.12	0.20	0.23	0.20	0.38	0.58	0.21	0.73
.25XA	5.29	7.3	0.08	0.10	0.08	0.10	0.19	0.28	0.10	0.34
.25XB	5.23	7.4	0.06	0.11	0.09	0.12	0.19	0.33	0.10	0.36
.25XC	5.20	7.8	0.07	0.11	0.09	0.13	0.19	0.35	0.10	0.36

Table IV-3. Analytical results for bucket testing of synthetic standards. Specific conductivity in µS corrected to 25°C, major ions in mg ℓ^{-1}, P_{tot} in µg ℓ^{-1}. Anion and cation sums in µeq ℓ^{-1}.

	Test Standard 1				Test Standard 2			
	Before		After		Before		After	
	1st analysis	2nd analysis	1st analysis	2nd analysis	1st analysis	2nd analysis	1st analysis	2nd analysis
pH	5.56	4.68	4.42	4.46	5.21	4.81	4.57	4.48
H	2.8	20.9	38.0	34.7	6.2	15.5	26.9	33.1
Cond	25.1	29.3	45.6	45.6	49.2	53.5	64.0	64.8
Na	--	0.10	0.35	0.29	2.51	3.21	2.50	3.15
K	--	2.71	3.23	2.73	3.37	2.82	4.32	2.86
NH_4	0.65	0.73	0.63	0.55	--	1.18	1.23	1.05
Ca	0.34	0.46	0.96	1.02	0.84	1.08	1.30	1.49
Mg	N.D.	N.D.	0.28	0.33	N.D.	N.D.	0.06	0.05
Cl	--	0.72	3.45	3.64	--	5.95	--	7.40
NO_3	--	0.98	1.02	1.00	--	1.03	--	0.97
SO_4	--	1.24	1.23	1.20	--	2.12	--	2.06
P_{tot}	--	--	1.98	--	16.6	--	0.5	--
Σ+		158	252	212		366		397
Σ-		168	247	249		374		406
Σ+/Σ-		0.94	1.02	0.85		0.98		0.98

N.D. not detectable

-- not analyzed

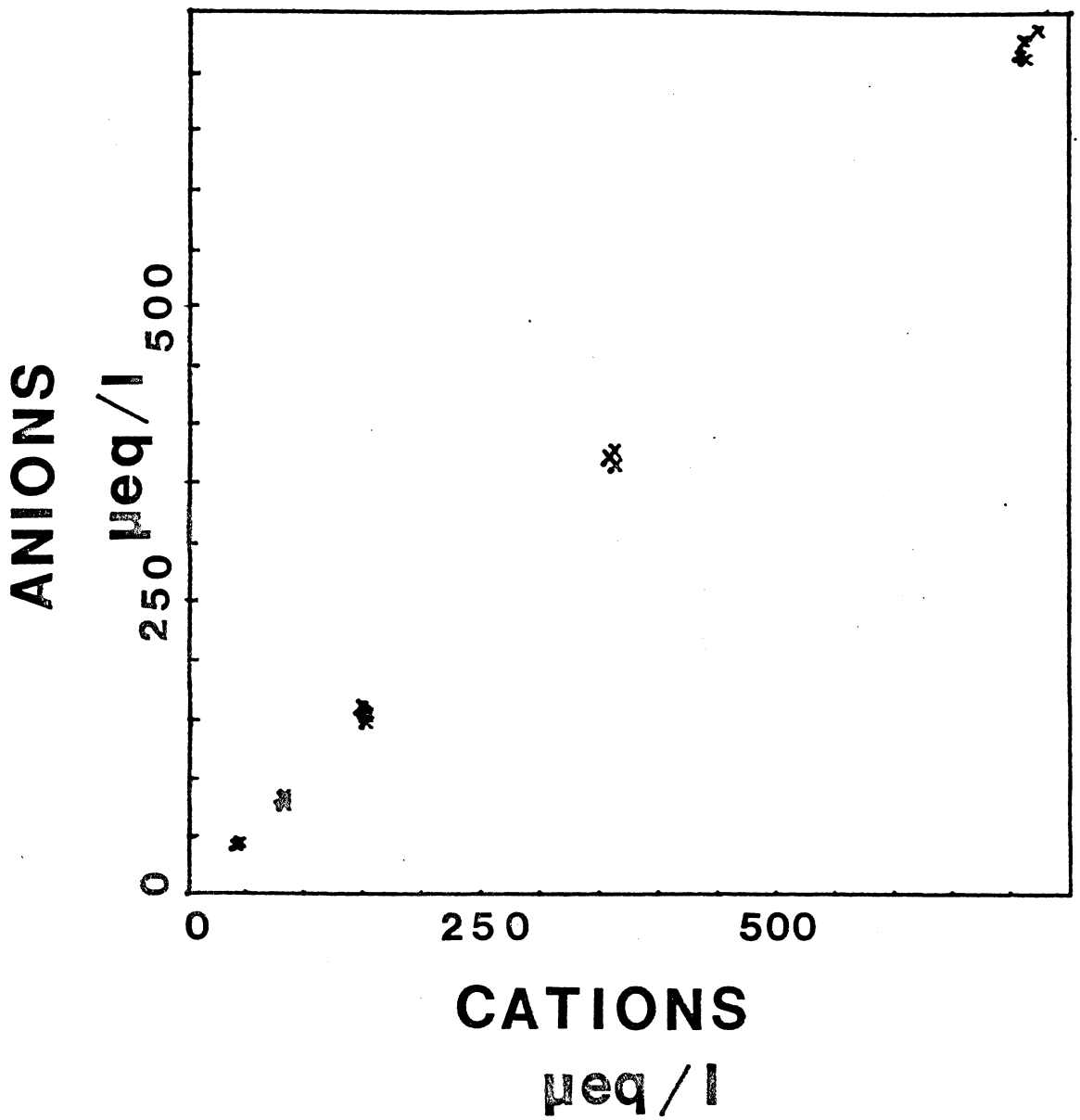


Fig. IV-1. Sum of anions vs. cations in serial dilutions of synthetic precipitation standards.

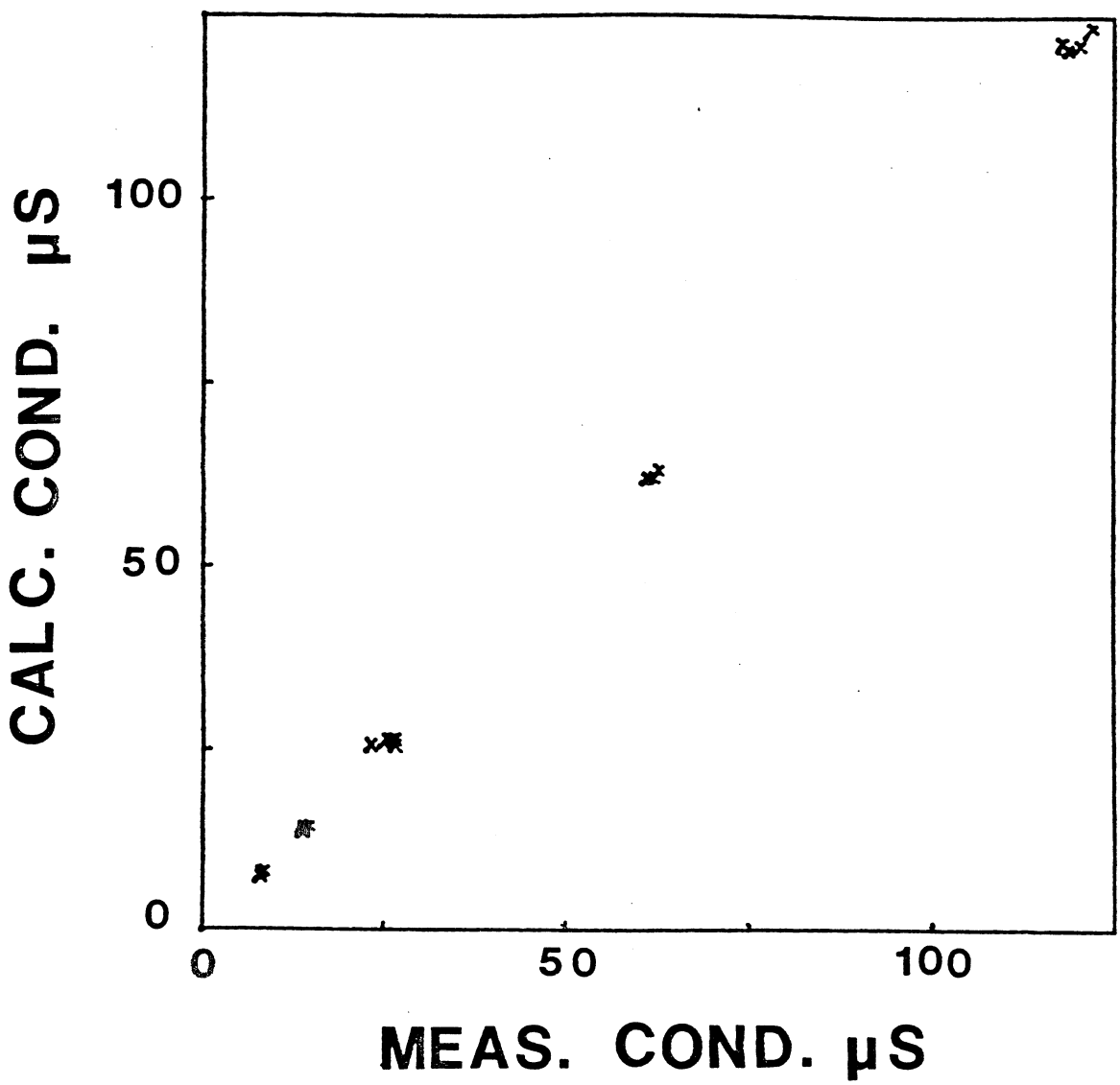


Fig. IV-2. Specific conductivity calculated from equivalent conductances and ionic concentrations in serial dilutions of synthetic precipitation standards vs. measured specific conductivity at 25°C.

Table V-1. Mean, range, and partial frequency distribution of anion/cation ratios in precipitation and dilute lakewater samples.

Site	mean	range	.9≤ x≤1.1*	.8≤x ≤1.2*	Reference
Hovland	0.99	0.46-2.28	26	58	This study
Itasca	0.98	0.31-1.93	37	64	" "
Tewaukon	1.04	0.49-3.15	33	63	" "
1978 snows	0.96	0.46-4.48	25	48	" "
78-79 snows	0.94	0.72-1.23	65	87	" "
Dilute Lakewater	0.99	0.31-1.58	38	56	Gorham and Dean (unpubl)
NADP precipitation	1.10	0.80-2.21	47	82	NADP (1978)

* Number of samples, expressed as % of samples completely analyzed.

Fig. V-ia-e. Plots of Anion/Cation ratios vs. specific conductivity in samples from a. Tewaukon, b. Itasca, c. Hovland, d. 1978-Snow, e. 1978-79 snow.

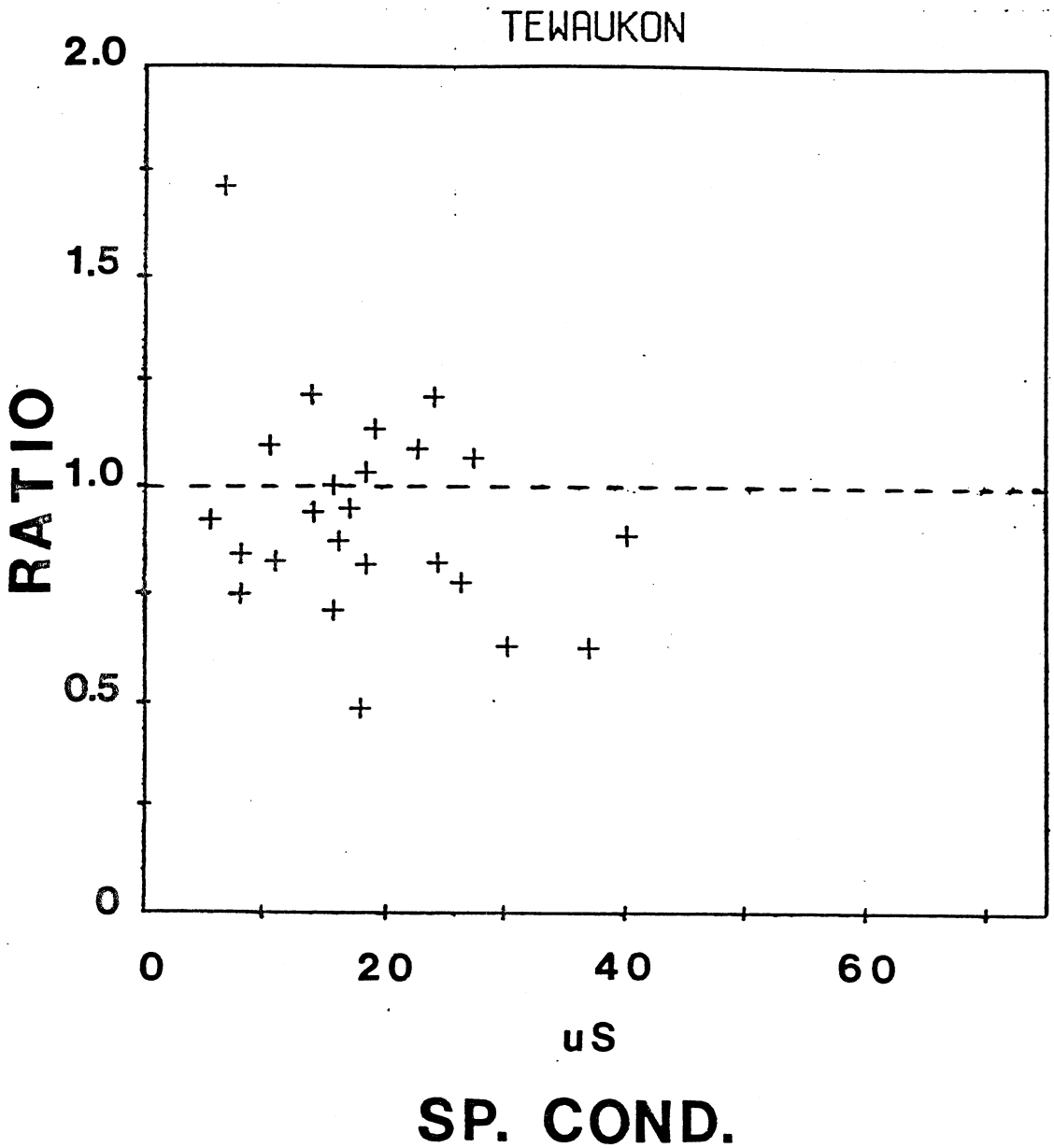


Fig. V-1a.

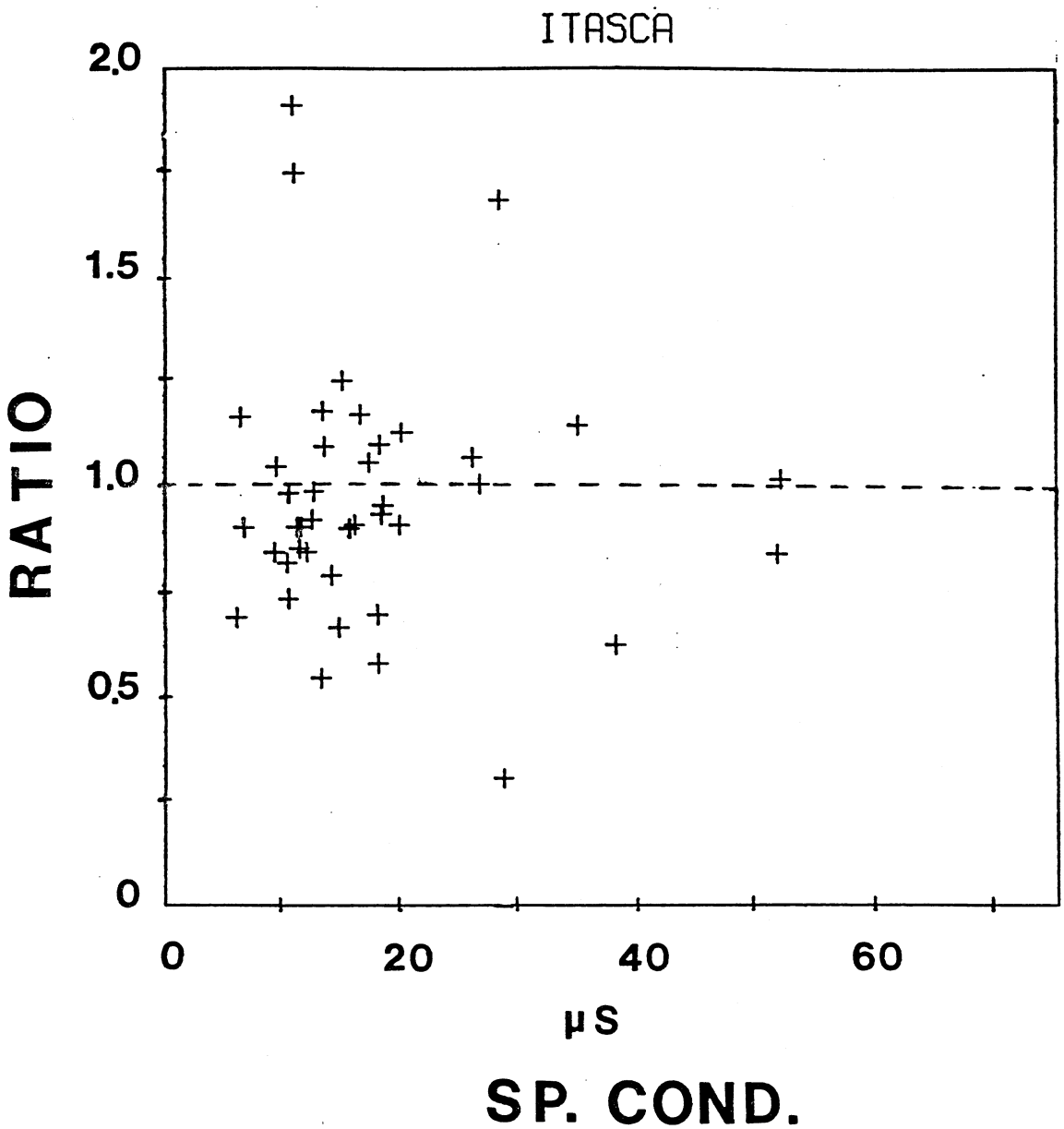


Fig. V-1b.

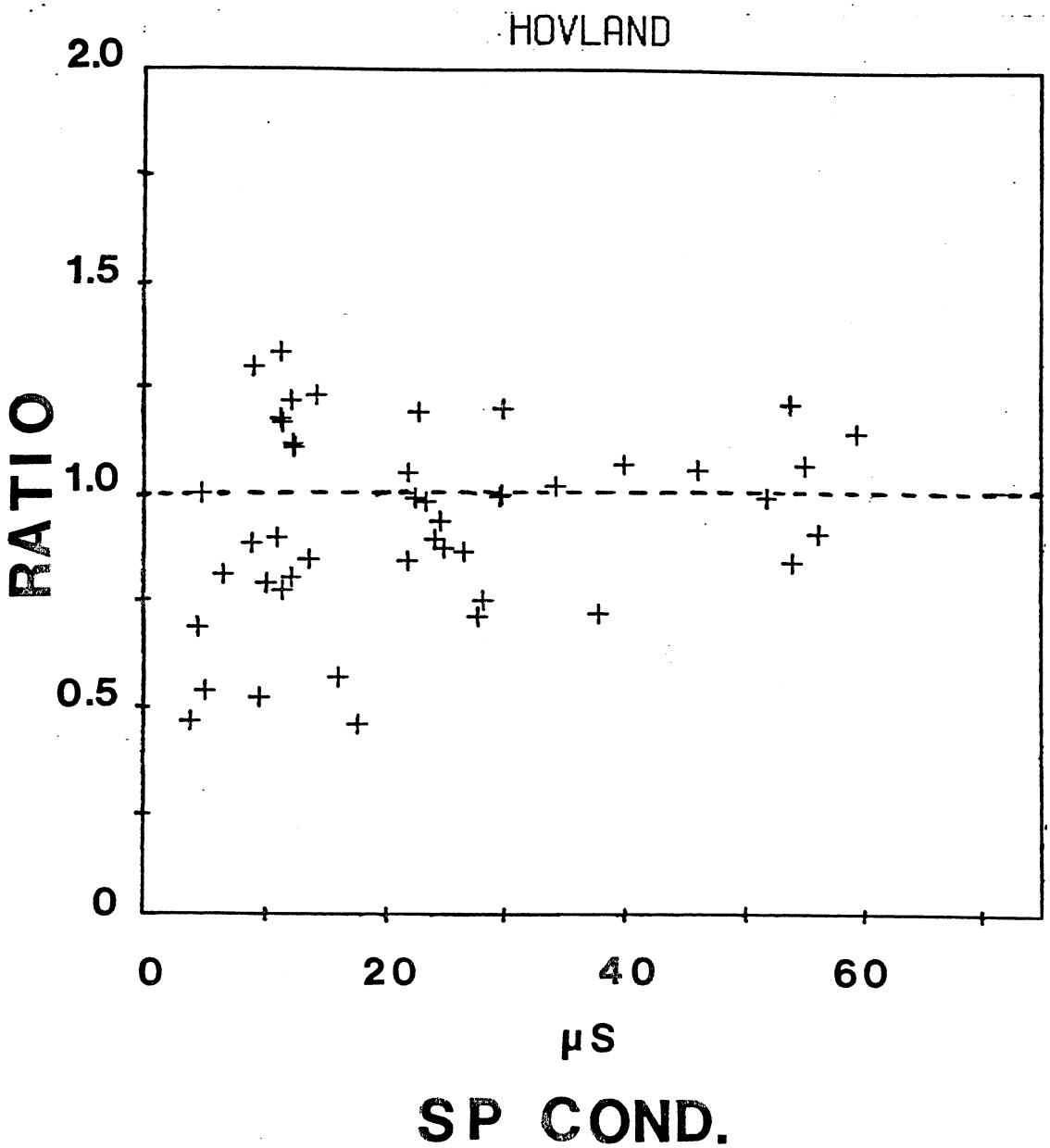


Fig. V-1c.

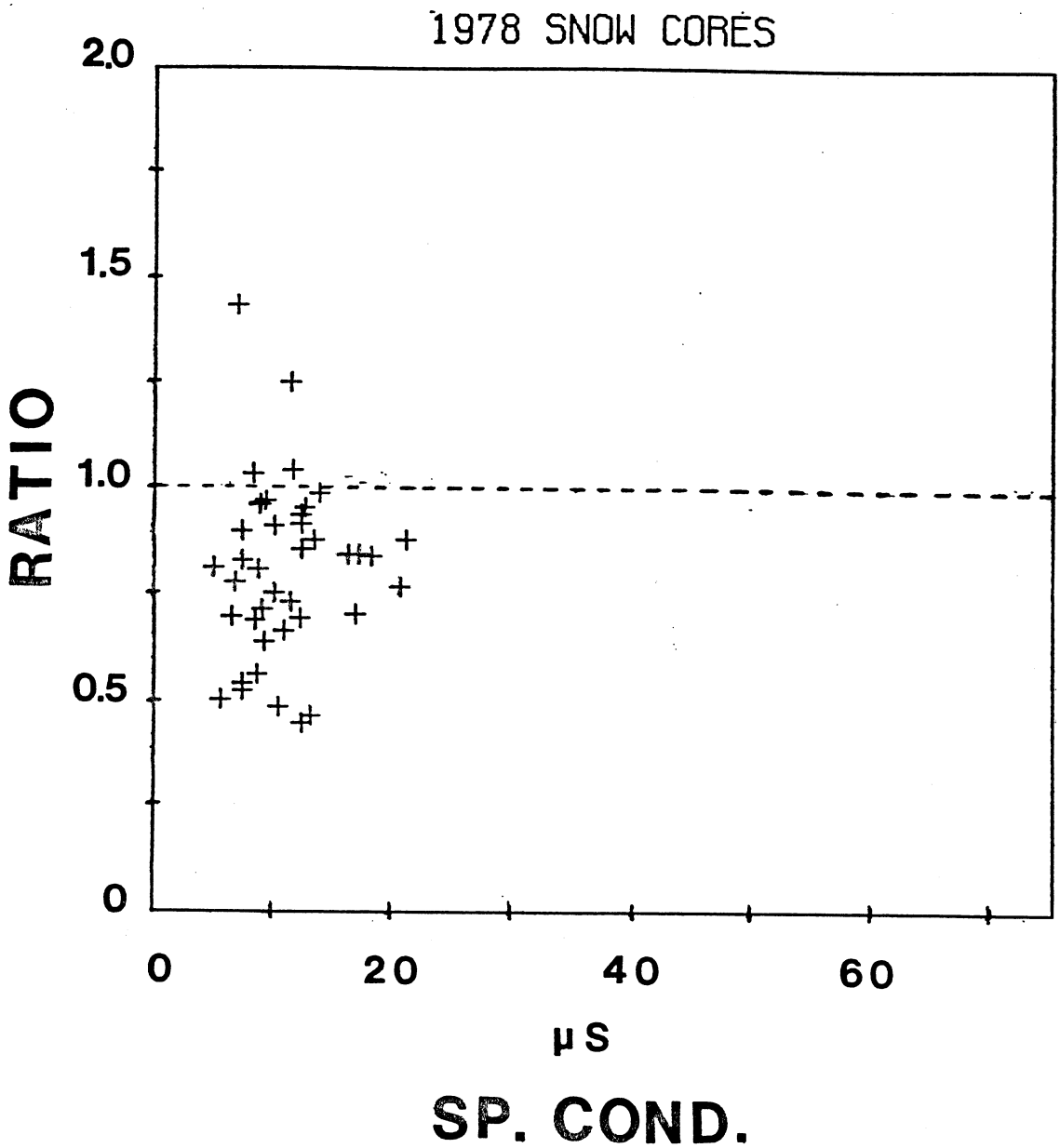


Fig. V-1d.

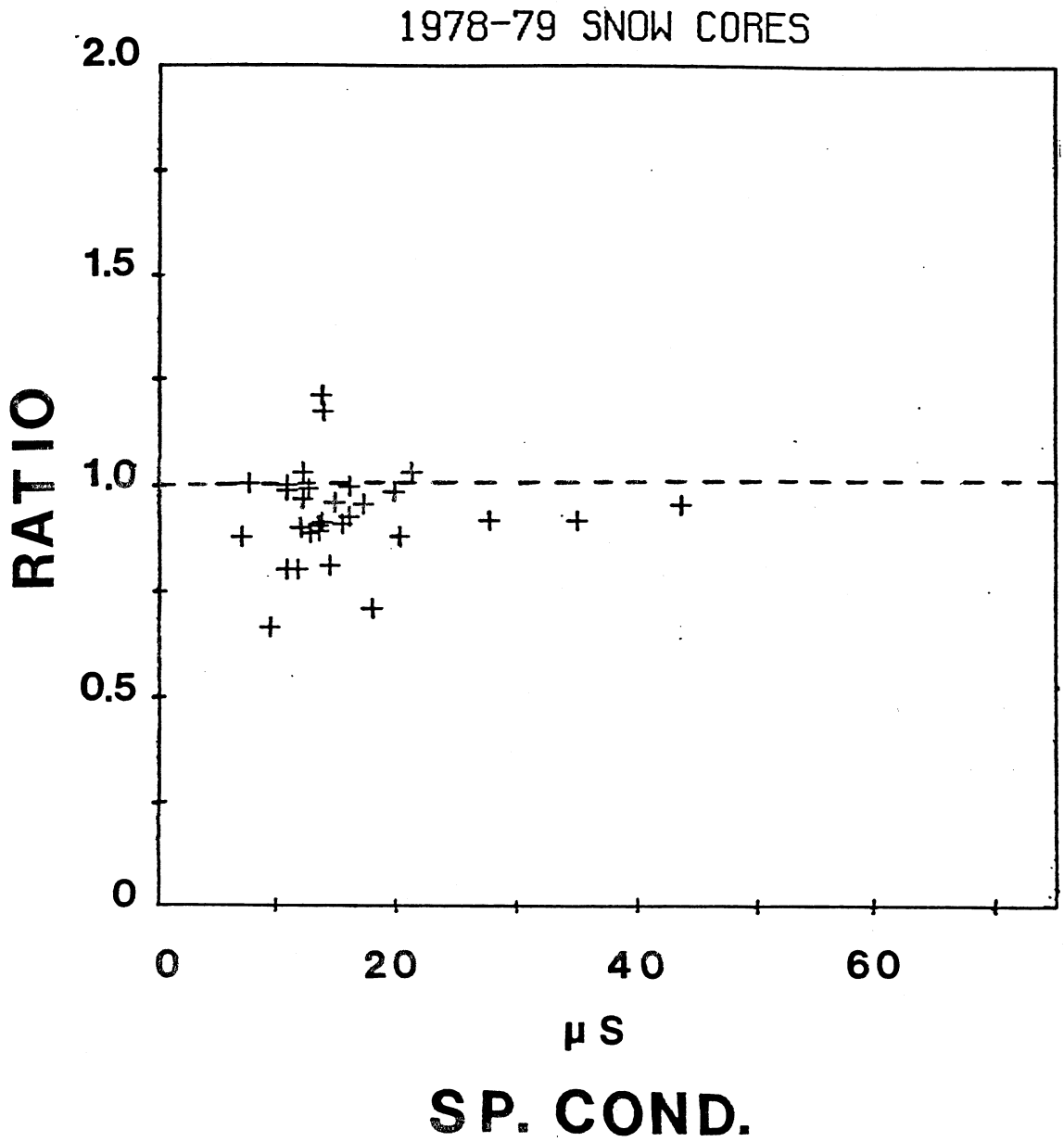


Fig. V-1e.

Appendix 6

Variable names, explanation of data codes, and raw data for samples of precipitation events collected at the three sites. Table 1 presents Tewaukon data, Table 2 the Itasca data, and Table 3 the Hovland data.

HEADING	MEANING
PH	pH
COND	Specific Conductivity at 25°C in μS
CL	Cl^- $mg\,\ell^{-1}$
NO3N	NO_3^--N "
SO4S	$SO_4^=$-S "
NA	Na^+ "
K	K^+ "
CA	Ca^{++} "
MG	Mg^{++} "
NH4N	NH_4^+-N "
TP	Total P $\mu g\,\ell^{-1}$
ALK	Alkalinity $\mu eq\,\ell^{-1}$ (measured by Gran Titration)
PART	Particulates $\geq$ 0.4 μm dry weight $mg\,\ell^{-1}$
LOSSIG	% loss on ignition at 500°C by particulate matter
DATE	Sample collection date mo/day/year
TYPE	Type of precipitation 0 = Rain 1 = Drizzle 2 = Thunder shower 3 = Freezing rain, sleet, or rain mixed with snow 4 = Snow flurries 5 = Light snow 6 = Heavy snow
DWIND, BWIND	Wind direction during event, wind direction before event 0 = Calm, no wind 1 = NE 2 = E 3 = SE 4 = S 5 = SW 6 = W 7 = NW 8 = N 9 = Varying 22 = Data not reported
DWINDS, BWINDS	Wind speed during event, wind speed before event 1 = Calm to light, 0-5 mph 2 = Moderate, 5-10 mph 3 = 10-20 mph 4 = High > 20 mph
TIME	Number of days since last precipitation event
LENGTH	Duration of event in hours

-0 indicates missing data

Table 1.

	PH	COND	CL	NO3N	SO4S	NA	K	CA	MG	NH4N	TP
1	6.65	24.10	1.65	.43	1.35	.74	.22	1.35	.32	.82	23.00
2	4.52	24.10	.43	.65	.78	.16	.23	.27	.06	-0	-0
3	6.15	18.10	2.10	.26	.62	.25	.10	.86	.37	.73	9.60
4	6.69	14.90	1.45	.39	.48	.22	.22	.97	.16	1.06	4.00
5	4.63	39.40	.35	.53	1.70	.43	.19	1.83	.27	1.16	8.00
6	6.22	19.50	4.60	.50	.62	.38	.36	1.53	.16	1.64	58.00
7	6.13	27.10	4.40	.44	.57	.88	.85	-0	.86	1.02	30.00
8	6.69	41.80	2.10	.69	1.25	1.07	1.17	-0	.79	.98	600.00
9	5.70	8.50	.62	.23	.28	.10	.07	.38	.08	.37	5.50
10	5.11	32.10	4.14	.07	.07	.60	.20	2.18	.31	.37	5.50
11	5.37	11.10	1.40	.32	.29	.18	.09	.58	.09	.30	8.20
12	5.48	29.40	3.50	.61	.52	.35	.48	1.27	.26	-0	-0
13	5.89	36.50	-0	.27	.29	.65	.14	2.66	.41	.39	19.40
14	6.20	11.80	.89	.63	.31	.25	.33	.93	.14	.54	10.50
15	6.19	16.70	2.20	.28	.48	.32	.32	.70	.30	.73	62.00
16	5.46	5.70	.41	.12	.13	.07	.13	.15	.06	.20	9.50
17	5.19	11.90	1.11	.24	.25	.30	.13	-0	.06	.45	7.70
18	5.80	26.00	4.20	.35	.60	.43	.63	1.89	.27	1.04	9.10
19	5.46	16.70	3.30	.21	.32	.40	.21	2.16	.18	.52	39.90
20	6.32	20.30	1.12	.34	.63	.17	.40	1.42	.27	.79	41.40
21	5.20	29.20	3.62	.38	.71	.37	.15	1.06	.40	.67	14.70
22	6.81	37.00	1.58	.64	.99	.36	1.14	4.22	.63	.02	125.00
23	6.83	28.00	.62	.44	.84	.37	.79	3.20	.38	1.05	156.00
24	6.39	28.70	1.12	.29	.36	.38	.18	-0	.34	-0	-0
25	4.21	33.70	1.12	.04	.15	.27	.16	-0	.04	.10	6.70
26	4.62	17.90	.35	.61	.20	.12	.10	-0	.03	-0	17.60
27	4.89	19.60	.24	1.04	.62	.12	.14	1.39	.42	.26	53.90
28	4.40	42.70	4.60	.69	.79	1.77	.12	1.26	.22	.74	11.40
29	4.89	14.80	.42	.42	.65	.10	.08	.34	.11	.30	8.28
30	5.91	12.10	.88	.35	.55	.14	.12	.47	-0	-0	4.75
31	5.91	7.00	1.86	.06	.14	.10	.04	.47	.08	.04	10.30
32	4.99	12.80	9.09	.17	.47	.08	.06	.40	.54	.21	2.00
33	6.07	6.80	1.64	.21	1.61	.23	.09	.47	.15	-0	8.20
34	4.93	10.10	.56	.41	.11	.12	.08	.70	.32	.36	16.80
35	4.89	35.50	3.47	.74	1.16	.15	.15	1.24	1.35	-0	22.70
36	6.53	25.60	.38	.69	1.23	.21	.19	.71	.12	1.74	16.40
37	6.22	66.10	1.23	1.86	3.66	.29	.30	2.17	.63	-0	36.70
38	6.00	21.30	1.42	.32	1.65	.39	.38	.93	.26	-0	9.90
39	6.32	12.20	.38	.30	.57	.27	.27	-0	-0	-0	32.20
40	6.70	17.20	.26	.41	1.12	.08	.32	.77	.14	1.52	49.60
41	7.42	49.80	1.48	.85	1.94	.28	1.29	-0	1.42	.91	249.00
42	6.36	14.00	.24	.28	.48	.09	.09	.63	.11	-0	20.20
43	6.42	10.40	.54	.29	.38	.09	.18	-0	-0	.74	16.20
44	6.03	17.10	.88	.46	1.04	.17	.14	.89	.23	1.10	22.80
45	5.59	8.50	.19	.24	.27	.06	.09	.21	.02	.45	21.60
46	6.40	9.30	.28	.25	.53	.04	.05	.49	.26	.75	-0
47	5.53	11.60	.85	.40	.48	.16	.11	.51	.16	.66	-0

Table 1.

	ALK	PART	LOSSIG	DATE	TYPE	DWIND	DWINDS	BWIND	BWINDS	TIME	LENGTH
1	40.	-0	-0	42078.	0	2.	4.	22.	-0	-0	18.0
2	-0	-0	-0	42478.	1.	2.	4.	7.	4.	4.0	40.0
3	18.	-0	-0	50978.	0	5.	3.	7.	4.	16.0	54.0
4	47.	-0	-0	51278.	0	2.	3.	3.	4.	3.0	16.0
5	0	-0	-0	51878.	0	5.	3.	3.	4.	6.0	4.0
6	35.	-0	-0	52278.	0	3.	3.	3.	4.	4.0	15.0
7	28.	-0	-0	52578.	2.	3.	4.	3.	4.	2.0	3.0
8	345.	-0	-0	53178.	2.	5.	3.	5.	3.	6.0	1.5
9	0	-0	-0	62278.	0	3.	2.	3.	4.	5.0	1.5
10	0	-0	-0	62678.	0	7.	4.	7.	4.	3.0	1.0
11	0	-0	-0	62878.	0	7.	3.	3.	3.	3.0	2.5
12	0	-0	-0	71078.	0	22.	-0	22.	-0	3.0	1.0
13	-0	-0	-0	71378.	2.	5.	2.	6.	3.	3.0	1.5
14	-0	-0	-0	71978.	2.	6.	3.	7.	3.	6.0	.3
15	25.	-0	-0	73078.	0	7.	4.	6.	3.	11.0	.3
16	6.	-0	-0	80178.	0	5.	4.	6.	3.	2.0	.3
17	0	-0	-0	81578.	0	5.	1.	3.	3.	14.0	12.0
18	9.	-0	-0	82378.	2.	0	2.	3.	3.	8.0	9.0
19	6.	-0	-0	82778.	0	1.	1.	7.	3.	4.0	1.0
20	98.	20.0	44.	91178.	0	3.	4.	7.	4.	15.0	7.0
21	0	16.8	62.	91878.	1.	1.	3.	7.	3.	7.0	14.0
22	-0	16.0	0	100678.	1.	6.	3.	9.	3.	19.0	18.0
23	137.	125.0	25.	111078.	3.	3.	4.	3.	4.	35.0	60.0
24	-0	-0	-0	11978.	5.	22.	-0	22.	-0	30.0	-0
25	0	1.6	0	12078.	4.	3.	4.	7.	3.	1.0	6.0
26	0	-0	-0	12678.	4.	4.	4.	7.	4.	1.0	10.0
27	0	34.0	13.	21978.	6.	3.	3.	7.	3.	18.0	9.0
28	0	8.0	20.	30178.	4.	8.	4.	3.	4.	12.0	-0
29	0	2.0	-0	31978.	0	7.	2.	7.	4.	18.0	15.0
30	-0	6.0	100.	32078.	0	7.	3.	7.	3.	1.0	4.5
31	3.	4.0	-0	32278.	3.	7.	2.	7.	3.	.4	14.0
32	0	8.0	92.	32978.	5.	1.	1.	4.	4.	8.0	10.0
33	-0	29.0	71.	33078.	3.	9.	3.	7.	-0	14.0	11.0
34	0	14.0	13.	41278.	2.	7.	3.	3.	4.	13.0	12.0
35	0	25.0	57.	41578.	1.	3.	3.	3.	-0	1.0	3.0
36	80.	3.2	-0	41978.	3.	7.	3.	3.	4.	4.0	5.0
37	-0	-0	-0	42578.	1.	1.	3.	7.	4.	5.0	4.0
38	12.	.8	-0	42678.	3.	4.	3.	7.	-0	1.0	6.0
39	-0	80.0	41.	50178.	0	7.	3.	7.	3.	5.0	9.5
40	-0	30.4	58.	50778.	0	3.	3.	1.	3.	3.0	55.0
41	240.	85.0	19.	51778.	2.	7.	-0	3.	3.	10.0	-0
42	47.	10.0	60.	52178.	0	5.	3.	5.	3.	4.0	.5
43	22.	13.0	56.	53078.	1.	7.	4.	5.	4.	9.0	16.0
44	12.	6.8	27.	61178.	0	3.	1.	7.	3.	12.0	2.0
45	0	8.0	40.	61278.	2.	7.	4.	3.	4.	10.0	48.0
46	-0	10.4	44.	70978.	0	1.	4.	3.	3.	16.0	1.0
47	0	3.3	40.	71278.	0	5.	2.	3.	3.	2.0	.5

Table 2.

	PH	COND	CL	HCO3	SO4S	NA	K	CA	MG	NH4N	TP
1	4.64	12.70	-0	.64	.20	.41	1.34	-0	.78	.11	3.20
2	4.44	24.90	.11	.16	.13	.17	-0	.06	.06	.26	5.00
3	4.52	27.00	-0	.56	1.31	.39	1.93	5.26	1.35	.85	7.90
4	4.48	13.70	.70	.35	.56	.08	.06	-0	.03	1.00	8.20
5	4.31	46.40	2.20	1.11	2.27	.30	.44	5.71	2.30	.48	46.60
6	5.00	43.00	-0	.18	.20	.20	.16	4.38	.32	.32	13.00
7	5.00	36.00	6.30	.15	.27	.64	.11	1.98	.26	.16	13.00
8	5.22	11.60	3.80	.09	.16	.23	.08	.70	.10	.13	6.00
9	5.30	11.20	0.70	.83	.60	.72	.11	4.94	.62	1.42	58.00
10	5.60	45.60	7.70	.26	.40	.94	.19	3.24	.57	-0	-0
11	5.12	14.20	1.43	.42	.64	.17	.10	.60	.16	.02	12.00
12	6.31	31.40	.63	.37	.49	.79	.13	2.48	.57	1.12	14.60
13	4.70	14.00	3.70	.08	.34	.20	.08	.45	.06	.53	1.70
14	4.70	14.00	.09	.40	.48	.21	.20	.34	.07	.49	8.90
15	6.41	14.60	.48	.39	.70	.15	.21	1.30	.11	.75	20.90
16	5.13	9.80	.67	.43	.26	.14	.18	.32	.10	.28	9.47
17	5.66	4.90	.26	.15	.15	.04	.02	.12	.02	.30	4.80
18	4.65	28.20	1.84	.63	.72	.31	.24	1.04	.14	.52	8.60
19	4.71	37.60	4.60	.25	.40	.47	.20	2.44	.37	.32	11.80
20	5.01	27.50	5.70	.08	.53	.30	.19	1.11	.67	.30	8.20
21	5.86	14.40	1.60	.91	.67	.07	.19	.61	.15	-0	19.40
22	4.82	38.10	7.46	.37	.64	.63	.31	2.67	-0	-0	-0
23	5.00	30.20	.30	.22	.47	.26	.04	1.15	.76	.18	7.00
24	5.00	7.00	.88	.11	.16	.11	.07	.26	.12	.22	28.00
25	5.84	12.00	.57	.34	.56	.07	.12	.63	.16	.08	15.60
26	4.92	6.90	.67	.13	.13	.10	.10	.22	.09	.68	9.90
27	6.16	9.50	1.91	.63	.41	.08	.06	.34	.07	.66	20.40
28	4.99	11.80	.27	.66	.38	.07	.04	.13	.04	.43	6.90
29	4.26	19.30	.29	.32	.65	.05	.07	.07	.02	.55	-0
30	5.77	8.30	.03	.10	.22	-0	-0	.29	-0	-0	-0
31	5.88	7.10	.63	.12	.21	.11	.24	.49	.10	.58	9.90
32	5.18	10.90	.74	.25	.46	.12	.21	.32	.08	.57	39.30
33	6.31	9.80	-0	-0	-0	.16	-0	-0	-0	-0	-0
34	4.96	14.10	-0	.12	.29	.17	.15	.48	.10	.25	7.80
35	4.60	17.40	2.10	.11	.26	.17	.03	.50	.10	.06	3.70
36	5.16	21.20	5.24	.09	.14	.55	.05	1.70	.24	.09	4.70
37	5.72	14.00	2.85	.36	.89	.15	.07	.35	.09	1.12	36.00
38	5.03	9.20	2.40	.19	.61	.08	.14	.39	.09	-0	14.50
39	5.11	8.50	.22	.09	.15	.08	.05	.20	.02	.11	7.80
40	5.07	9.30	.49	.16	.28	.10	.10	.42	-0	-0	-0
41	5.98	9.00	.49	.29	.29	.10	.09	.38	-0	.60	7.70
42	5.03	18.20	2.35	.16	.32	.34	.07	.75	.21	.16	11.80
43	4.68	19.00	1.29	.43	.35	.19	.14	.51	.06	.18	15.80
44	4.98	14.00	1.45	.28	.42	.11	.11	.42	.20	.03	5.00
45	5.78	21.00	4.10	.36	.31	.21	4.32	-0	.08	.02	18.90
46	4.52	24.00	1.31	.07	1.12	.21	-0	.25	.08	.27	39.00
47	4.85	11.00	.08	.17	.12	.08	.09	.08	-0	-0	1.00
48	4.72	11.00	.44	.29	.29	.06	.02	.23	.14	.09	4.90
49	4.60	11.00	.56	.42	.12	.16	.24	.40	.24	.02	50.00
50	5.79	10.00	.63	.45	.42	10.50	1.90	.87	.03	.11	-0
51	4.47	10.80	1.79	.36	.32	.21	.11	.75	.08	-0	18.30
52	4.44	14.00	.21	.46	.19	.10	.13	.63	.15	.05	13.80
53	4.72	13.90	.54	.32	.14	.11	.08	.23	.20	.03	6.60
54	4.43	13.00	.55	.42	.47	.07	.05	.11	.09	.11	9.80
55	4.53	19.10	1.07	.42	.23	.09	.04	1.53	.07	.34	1.60
56	5.66	11.00	1.00	.25	.48	.11	.03	.39	1.01	.30	4.90
57	5.23	10.90	1.32	.67	.89	.16	.09	.48	.58	.93	7.70
58	5.13	10.70	.95	.66	.47	.06	.06	.12	.19	.03	2.00
59	4.56	24.00	2.55	.60	.75	.15	.11	.96	.39	.32	12.60
60	4.52	42.60	11.00	.31	.75	.44	.14	1.27	1.09	-0	8.90
61	4.30	17.00	1.15	.34	1.04	.11	.07	.46	.60	.77	5.10
62	4.48	45.40	4.10	.62	.08	.27	.15	1.03	2.17	.06	10.20
63	6.08	24.50	1.87	.69	1.10	.25	.17	1.58	-0	-0	10.30
64	6.01	46.00	1.41	.30	.64	.38	.07	.57	.46	.98	6.30
65	5.64	49.70	11.80	.66	2.53	.14	.30	1.58	2.96	.10	9.70
66	5.51	7.70	0.04	.13	1.40	.10	.09	.62	.10	.41	3.30
67	6.14	12.60	.45	.29	.49	.29	.09	.58	.10	.01	10.20
68	6.12	13.00	1.48	.20	.36	.15	.14	1.18	1.44	.24	10.10
69	6.48	14.00	.76	.26	.85	.06	.10	.34	.32	-0	11.70
70	5.68	15.00	.35	.39	.60	.07	.08	.67	.16	1.06	38.50
71	5.20	11.10	.38	.22	.36	.06	.03	.28	.08	.50	9.00
72	6.88	54.90	7.60	.54	1.01	5.57	3.34	1.43	.32	2.14	52.90
73	6.59	12.10	.78	.54	.62	.05	.19	.80	.17	.87	35.50
74	6.58	12.10	.74	.46	.49	.10	.02	.75	.18	.34	30.00
75	4.90	12.10	.19	.20	.57	.09	.03	.34	.02	.34	16.30
76	4.88	13.20	.07	.21	.55	.08	.04	.35	.06	.34	4.10
77	4.90	13.30	.07	.21	.62	.10	.04	.39	.03	.45	7.90
78	6.26	11.30	.49	.22	.35	.22	.30	.25	.04	1.07	-0
79	5.78	8.90	-0	-0	-0	-0	3.14	.34	.24	.18	-0

Table 2.

	ALN	PART	LOSSIG	DATE	TYPE	EWIND	DWINDS	BWIND	PWINDS	TIME	LENGTH
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2											
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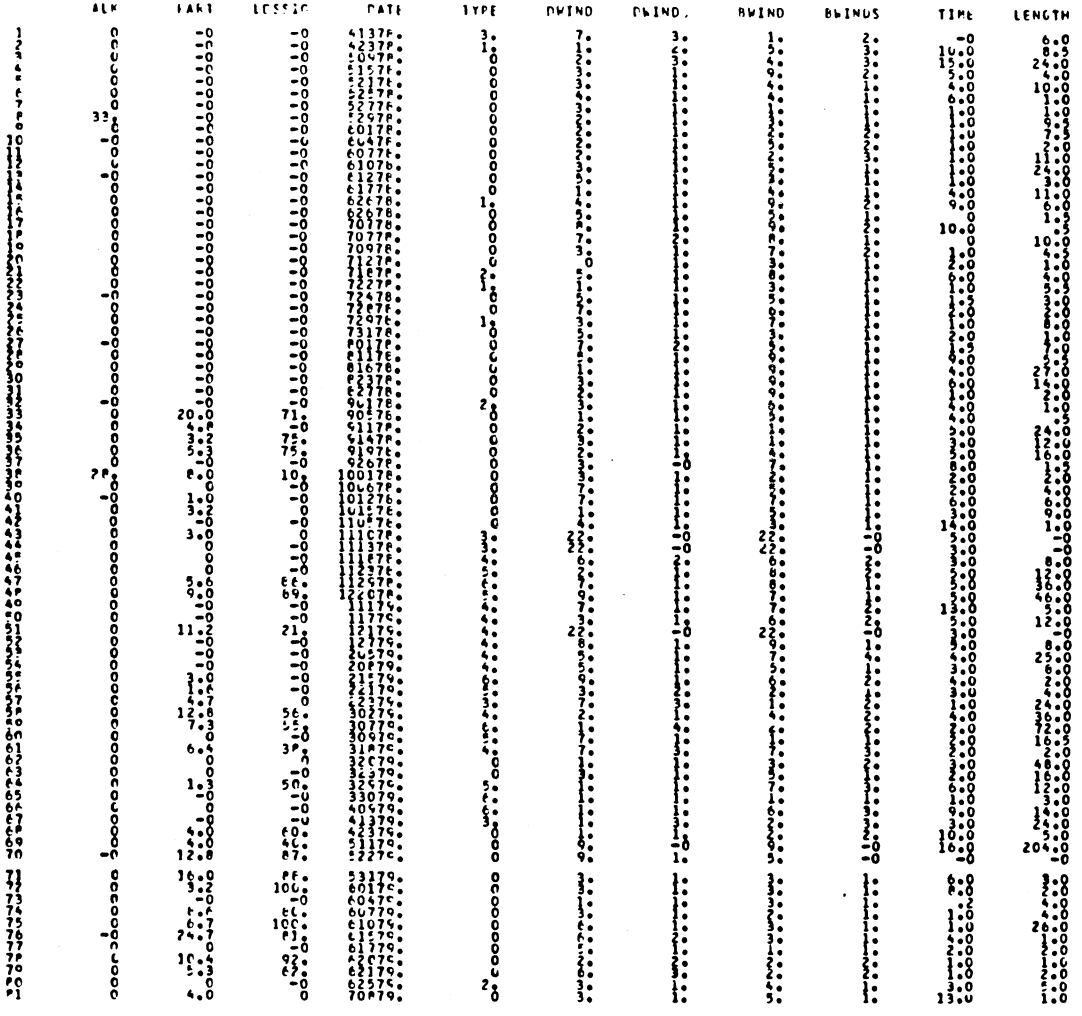
Table 3.

	PH	COND	CL	NO3N	SO4S	NA	K	CA	MG	NH4N	TP
1	4.85	15.70	-0	.23	.73	.09	.06	.20	.02	.41	12.30
2	4.10	41.40	-0	-0	-0	-0	-0	-0	-0	-0	-0
3	4.45	23.50	.15	.66	.74	.11	.04	.08	.11	.23	4.60
4	4.48	17.40	-0	-0	-0	-0	-0	-0	-0	-0	-0
5	4.00	16.00	.18	.34	2.22	.12	.02	.14	.04	.59	4.70
6	4.80	9.70	.62	.16	.46	.03	.08	.14	.01	.07	3.40
7	4.70	22.90	-0	.16	.81	.31	.44	.13	.16	-0	-0
8	4.78	13.20	1.01	.17	.88	.10	.53	.06	.06	1.97	183.60
9	4.65	13.60	-0	.18	.46	.06	.66	.06	.01	.17	3.00
10	4.80	10.40	.24	.20	.53	.11	.75	.44	.16	.39	45.60
11	4.48	7.10	.55	.10	.25	.08	.02	.16	.04	.15	7.30
12	4.00	63.50	.39	.26	2.67	.09	.24	.40	.12	.61	37.00
13	6.19	12.60	.98	.44	.62	.11	.28	.44	.16	.91	51.40
14	4.62	26.70	3.30	.44	.90	.67	.14	1.62	.28	.42	27.60
15	4.58	56.90	3.20	.23	.73	.46	.05	.90	.18	.48	2.30
16	4.93	12.10	1.47	.14	.23	.15	.03	.41	.06	.06	2.27
17	4.00	92.50	16.00	.03	1.03	-0	-0	-0	.54	-0	-0
18	4.93	4.74	.55	.07	.06	.05	.08	.15	.01	.04	3.98
19	4.81	13.40	1.55	.12	.26	.19	.08	.22	.07	.07	3.00
20	4.23	62.30	1.60	.22	1.02	1.11	.22	3.94	.28	.59	4.50
21	4.81	15.10	.92	.40	.42	.08	.07	.18	.04	.30	3.60
22	4.22	57.60	9.60	.39	.64	.64	.09	2.61	.39	.21	8.80
23	5.55	7.70	.84	.11	.19	.17	.18	.91	.07	.34	8.60
24	4.60	17.90	1.11	.21	.35	.14	.18	.25	.06	-0	13.60
25	4.72	12.30	.12	.26	.24	.03	.03	.09	.02	.28	9.60
26	4.58	26.30	.48	.24	1.36	.06	.10	.42	.09	1.20	8.80
27	5.88	6.80	.27	.21	.46	.06	.15	.32	.13	.83	11.20
28	5.23	11.80	1.42	.17	.29	.17	.10	.58	.12	.33	14.40
29	4.60	14.50	.18	.09	.78	.06	.08	.22	.04	-0	4.20
30	5.11	9.80	1.37	.10	.18	.20	.12	-0	.19	.13	5.60
31	4.69	104.00	26.00	.24	.66	1.66	.15	-0	1.78	-0	-0
32	5.50	17.60	1.74	.33	.55	.18	.07	.63	.55	.79	6.60
33	4.06	42.80	3.00	1.30	1.76	.29	.43	2.43	.82	-0	37.80
34	5.18	12.20	.75	.25	.60	.06	.08	.45	.04	.39	16.50
35	4.50	23.50	1.26	.24	.47	.23	.12	.61	.05	.25	6.00
36	4.32	32.00	1.44	.47	1.06	.18	.12	.42	.05	.45	14.50
37	4.29	11.30	-0	-0	-0	-0	-0	-0	-0	-0	-0
38	4.27	30.20	.68	.29	1.64	.22	.18	1.20	.24	1.77	45.30
39	4.71	10.20	.55	.65	.35	.26	.24	1.33	.04	.03	7.70
40	4.80	26.00	.74	.20	1.41	.40	.24	.91	.20	1.30	21.10
41	4.62	42.80	.67	.27	.31	.17	.12	.27	-0	.39	2.40
42	4.28	22.70	1.80	.27	1.31	.21	.17	1.37	.19	1.38	12.80
43	4.45	41.60	.60	.27	.79	.40	.15	1.86	-0	.25	7.00
44	4.68	16.20	3.30	.05	.36	.17	.03	.40	.06	.03	3.10
45	4.47	19.00	.44	.16	.62	.10	.11	.13	.02	1.02	3.20
46	4.62	12.30	.40	.22	.26	.10	.07	.06	.01	.04	3.20
47	4.38	24.50	1.16	.31	.59	.15	.08	.39	.09	.07	-0
48	4.37	22.10	.67	.16	.63	.10	.20	.18	.09	.29	4.20
49	4.17	47.20	2.77	.28	.65	.10	.28	-0	.09	-0	-0
50	4.42	26.90	-0	-0	-0	-0	.30	.10	-0	.06	.04	5.20
51	4.38	26.80	-0	.18	.77	.15	.04	.38	.05	.14	21.50
52	4.00	84.20	-0	-0	-0	-0	-0	-0	-0	-0	-0
53	4.22	33.80	1.17	.74	.33	.26	.08	-0	-0	-0	7.40
54	4.42	28.60	2.21	.46	.28	.58	.07	.64	.10	-0	-0
55	4.38	24.20	.24	.47	.28	.09	.01	.10	.01	.09	1.80
56	4.32	40.30	6.70	.40	.36	1.04	.11	2.40	.14	.14	1.40
57	4.11	40.50	.71	.35	1.11	.08	.06	.62	.05	.30	3.60
58	4.15	57.80	1.68	1.21	1.41	.30	.09	1.12	.06	1.32	7.50
59	4.50	28.40	1.35	.36	.70	.16	.07	.38	.17	-0	2.39
60	4.32	24.70	1.79	.39	.54	.21	.02	.40	.25	.20	2.60
61	3.61	156.50	1.11	3.64	5.04	.31	.19	.41	-0	-0	26.40
62	4.12	47.80	.90	.54	1.28	.23	.02	.14	.04	.52	4.60
63	4.22	31.80	.41	.35	1.03	.10	.01	.14	.08	.31	4.10
64	4.60	29.70	.27	.18	.25	.09	.10	.14	.00	.11	3.40
65	4.58	17.30	1.27	.17	.45	.23	.18	.10	.13	.10	1.00
66	4.70	15.30	1.39	.32	.43	.36	.03	.37	.07	.15	1.20
67	4.99	12.40	.72	.26	.64	.07	.03	-0	1.78	.13	16.00
68	4.51	22.50	.60	.50	1.03	.10	.10	.28	.06	.95	2.20
69	5.12	9.60	.24	.16	.47	.05	.03	.22	.02	.46	10.90
70	4.77	21.40	.62	.21	.92	.05	.02	.18	.30	2.87	518.00
71	4.39	26.60	.33	.41	1.11	.09	.22	.35	.07	.66	102.70
72	4.00	8.40	.24	.11	.25	.05	.02	.33	.27	.07	2.50
73	4.78	10.00	-0	-0	-0	-0	-0	-0	-0	-0	61.00
74	5.31	10.90	.24	.36	.70	.03	.03	.29	.16	.81	14.60
75	4.44	4.10	.24	.07	.29	.05	.22	.47	.23	.15	56.40
76	4.91	23.90	1.17	.79	1.67	.46	.38	2.00	.49	1.09	59.90
77	4.61	13.30	.30	.34	.30	.10	.04	.36	.02	.02	9.50
78	3.91	60.10	.31	.90	2.27	.13	.08	.44	.10	1.44	27.60
79	4.74	14.80	.10	.32	.22	.04	.18	.40	.04	.04	9.70
80	4.15	7.00	.14	.18	.19	.03	.05	.22	.03	.17	12.90
81	3.98	55.60	.55	.22	2.17	.09	.20	.60	.08	.64	-0

Table 3.



APPENDIX 7

FREQUENCY DISTRIBUTIONS

Figures VII-1a-j present the frequency distributions for major ions, P_{tot}, and specific conductivity. Bar height indicates the percent of samples having values within that interval. The figures illustrate shifts in modes and distributions about the mean that occur between the sites. The distributions are generally skewed to low values, which suggests a log-normal distribution as was observed in precipitation chemistry data collected by ACRES (1974). Distributions of log-transformed data (not shown) confirmed the log-normality of data from this study.

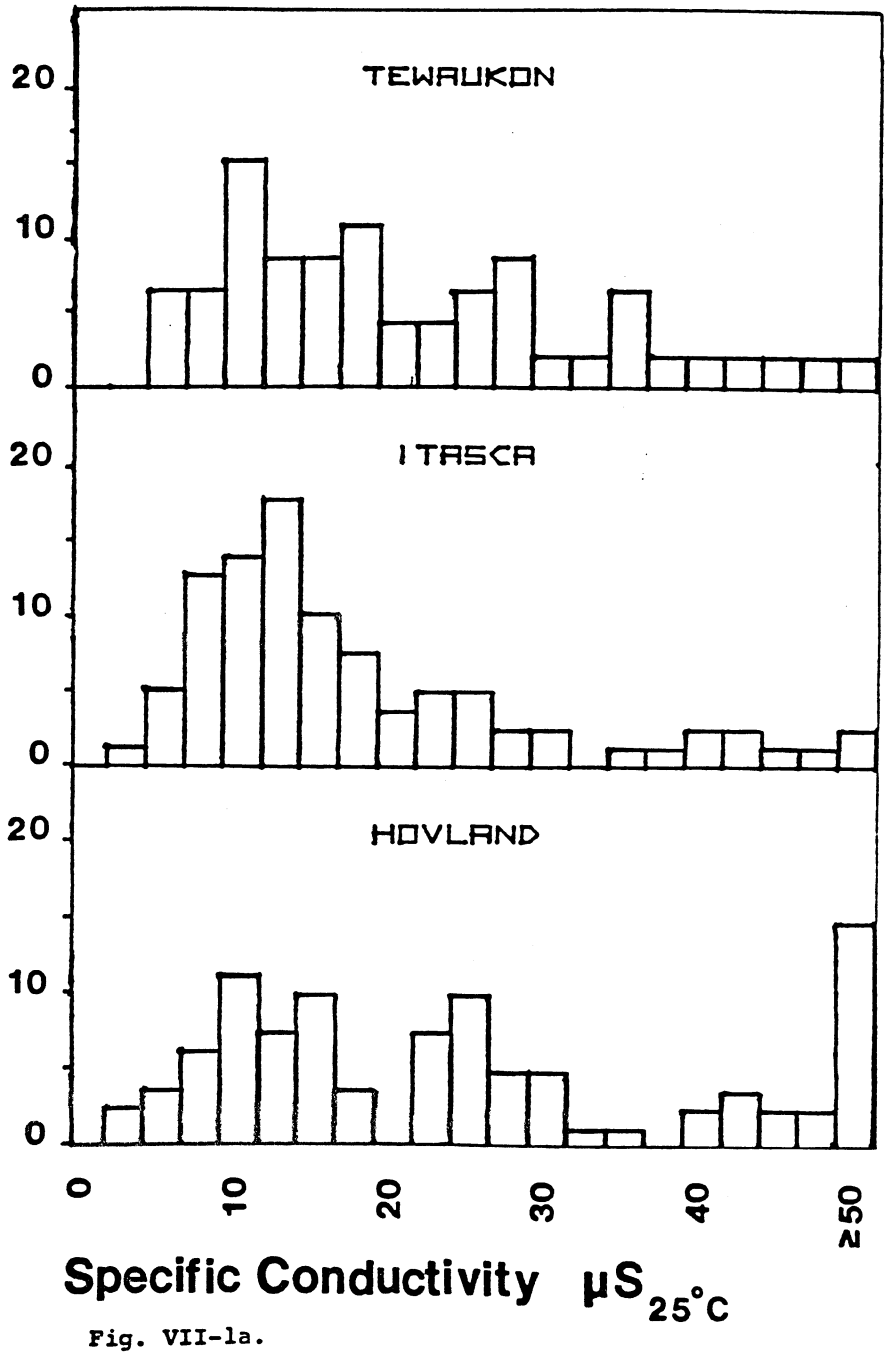

TEWAUKON
ITASCA
HOVLAND
20
10
0
0
10
20
30
40
≥50
Specific Conductivity μS25°C

Fig. VII-1a.

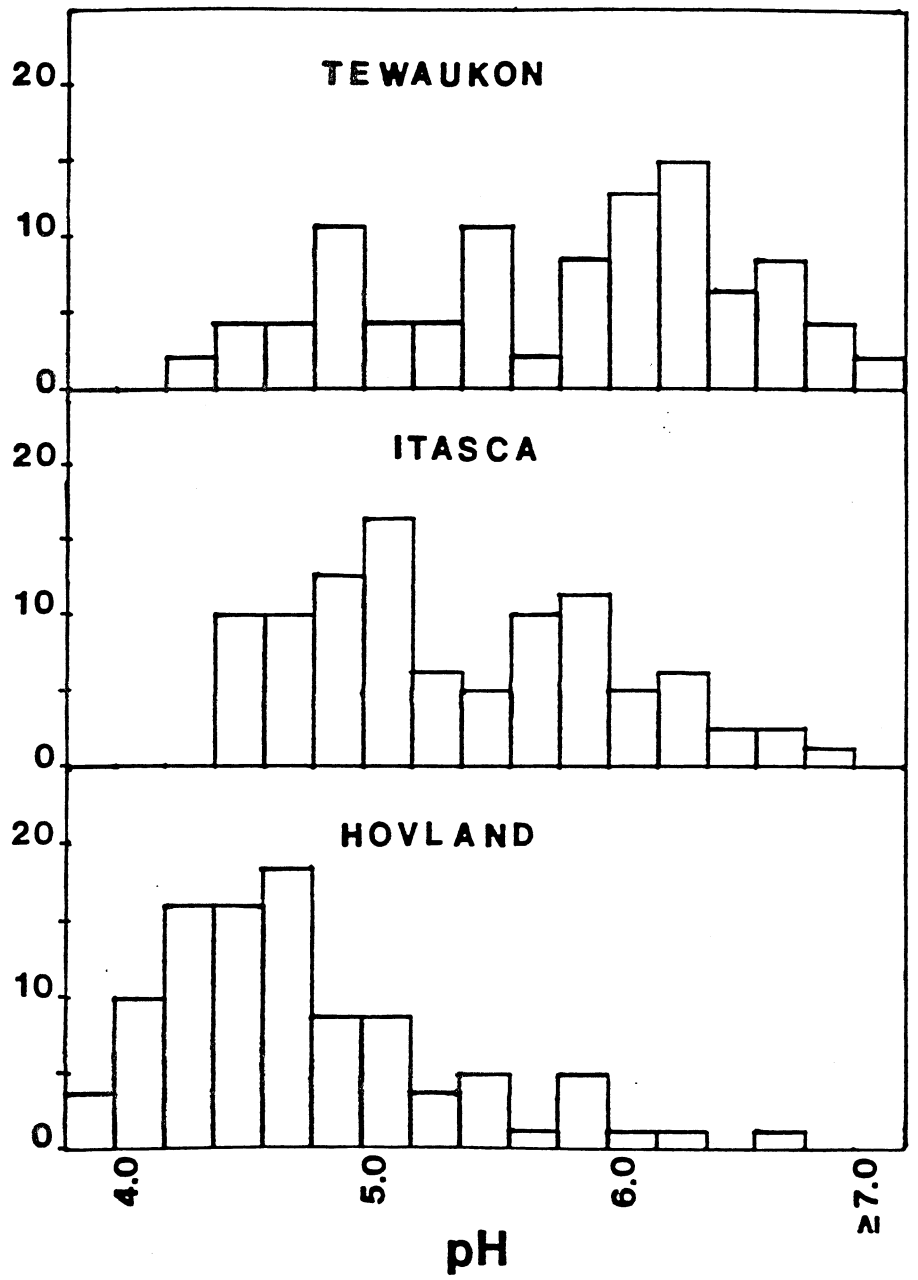


Fig. VII-1b.

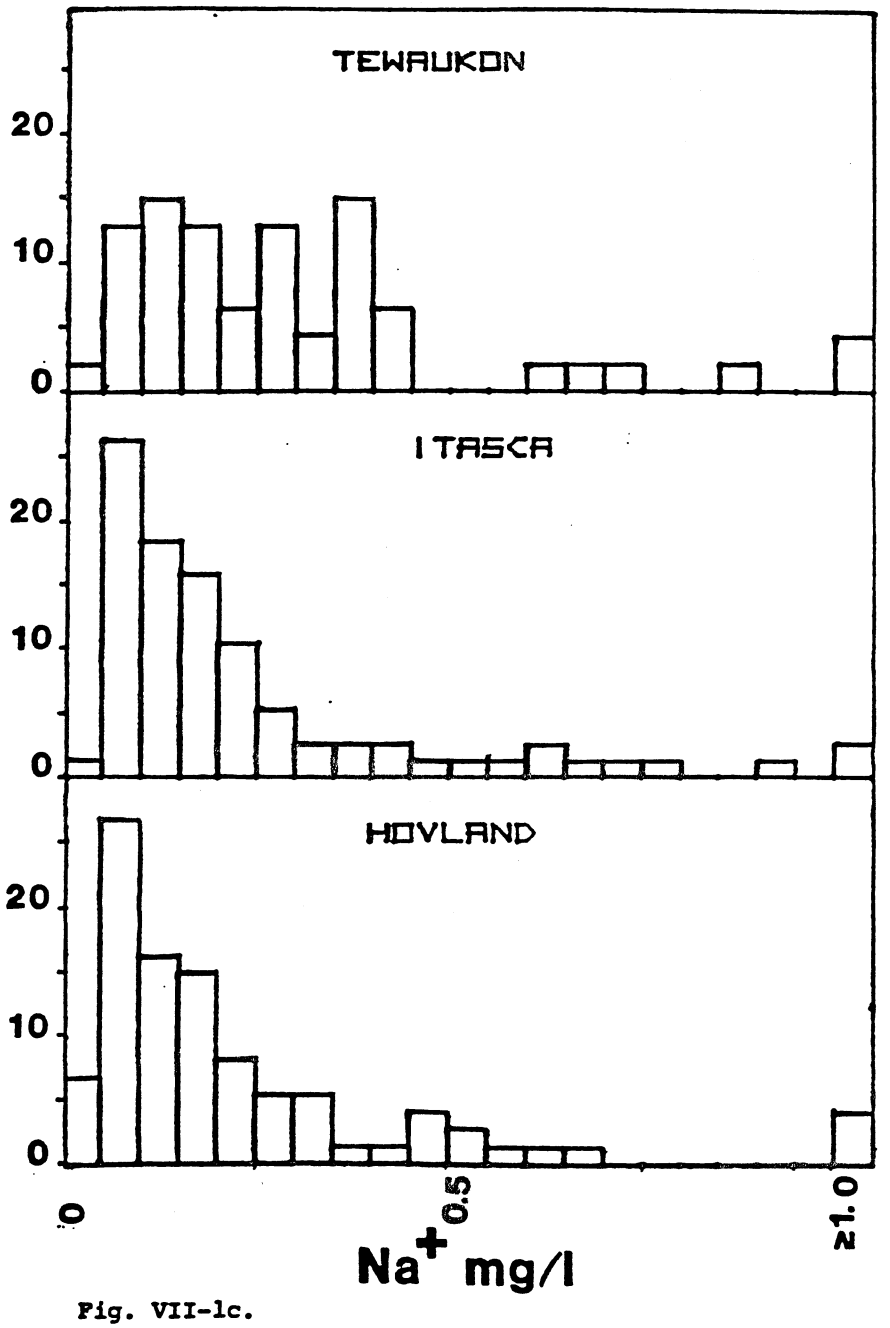


Fig. VII-1c.

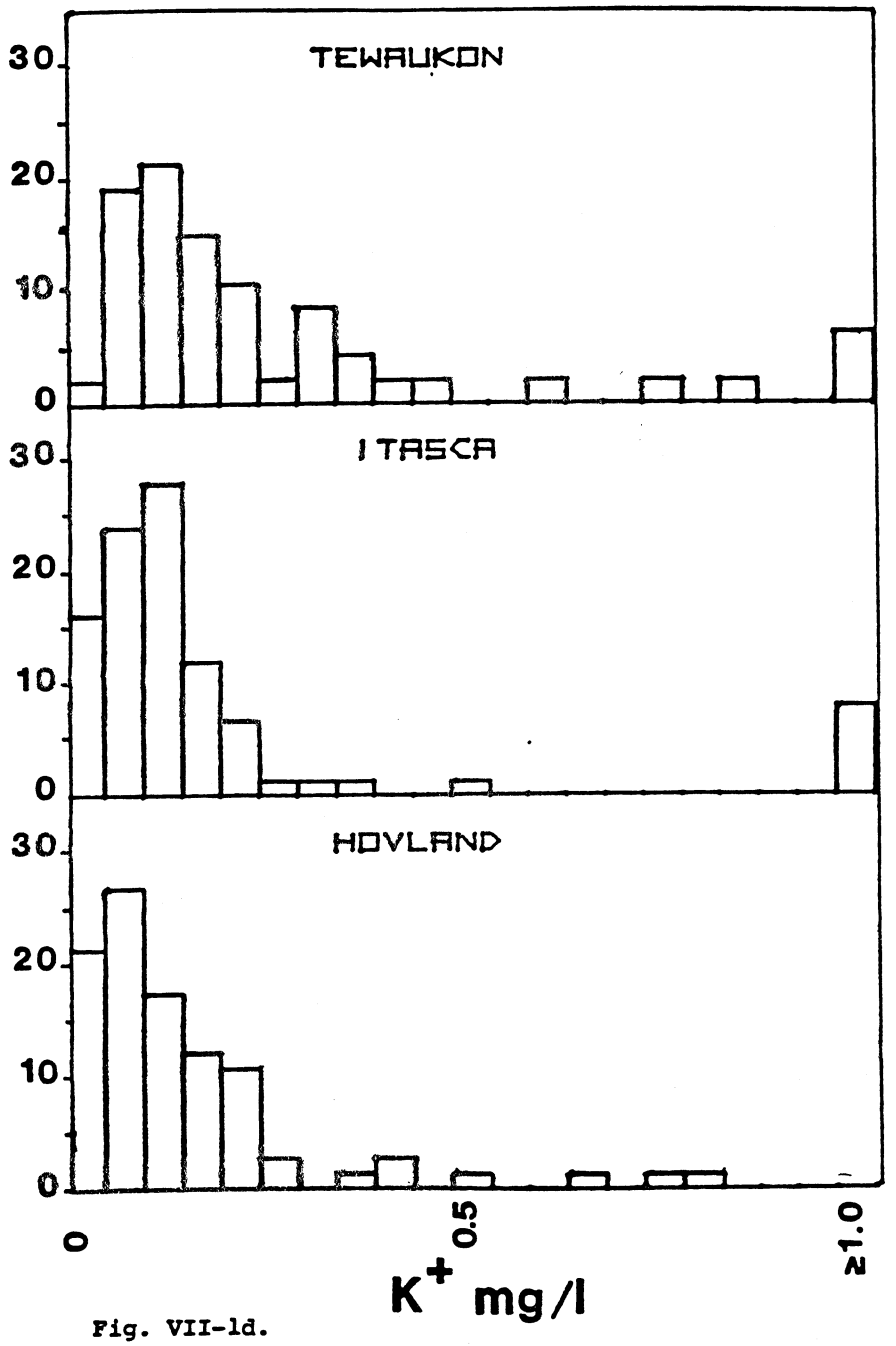


Fig. VII-1d.

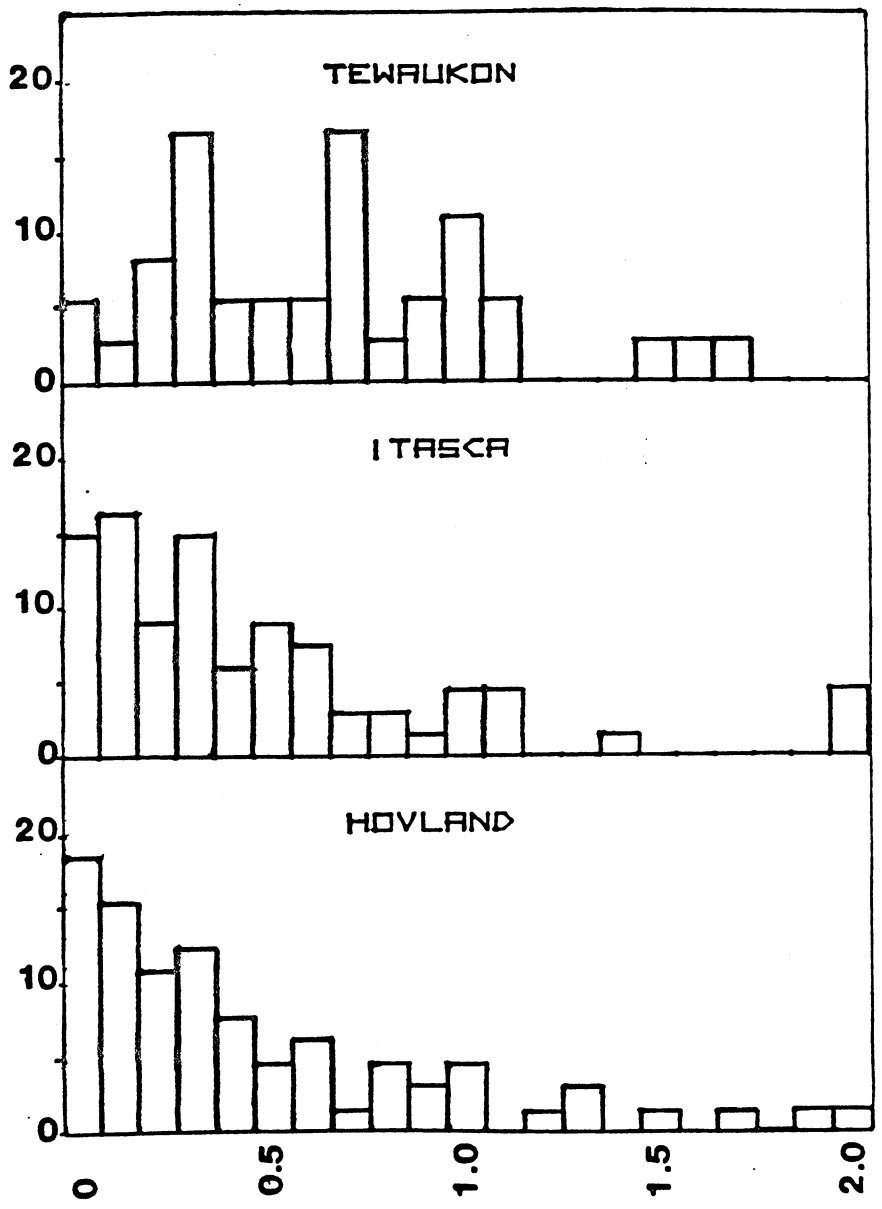


Fig. VII-1e. NH_4^+-N mg/l

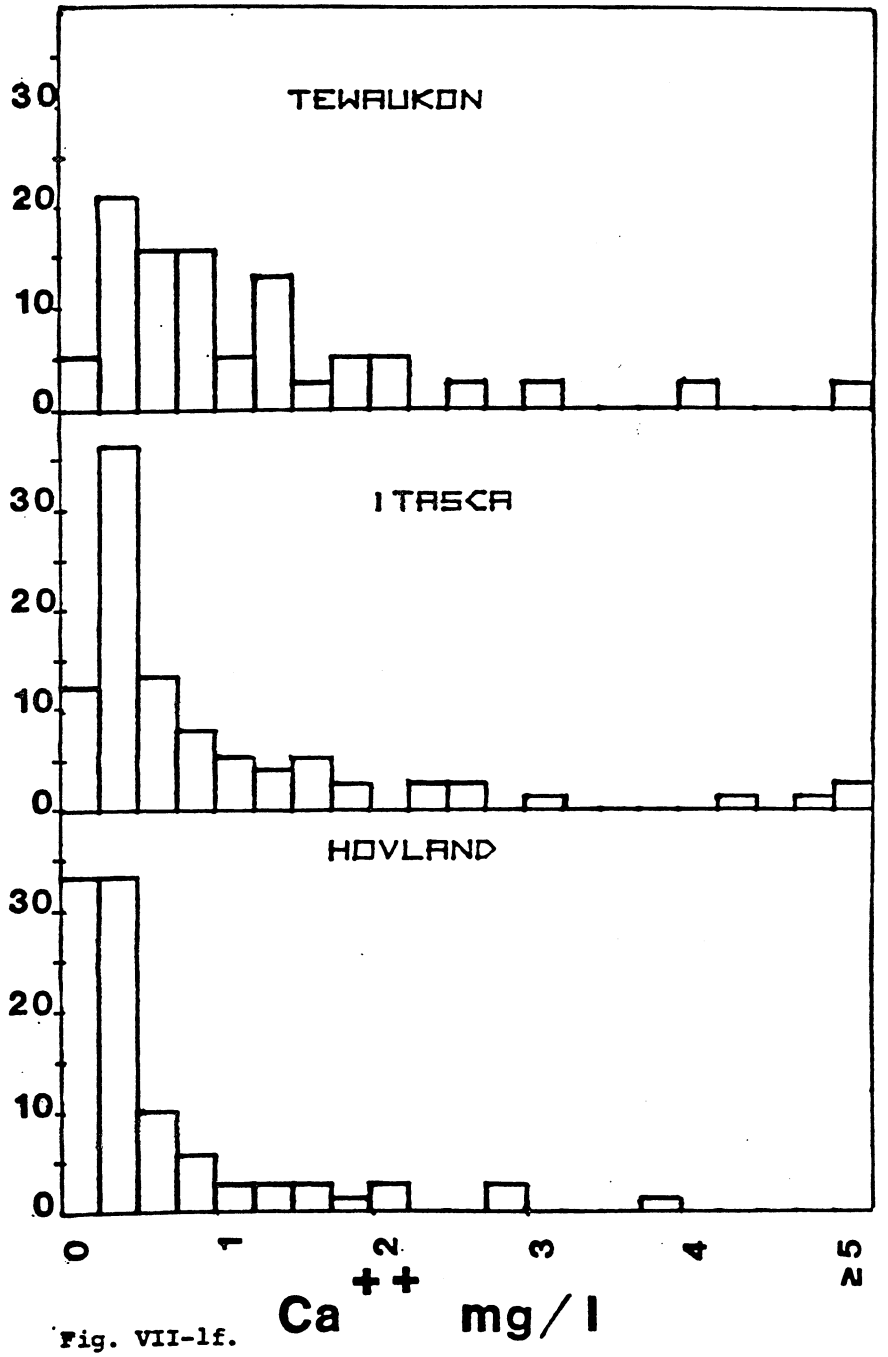


Fig. VII-1f.

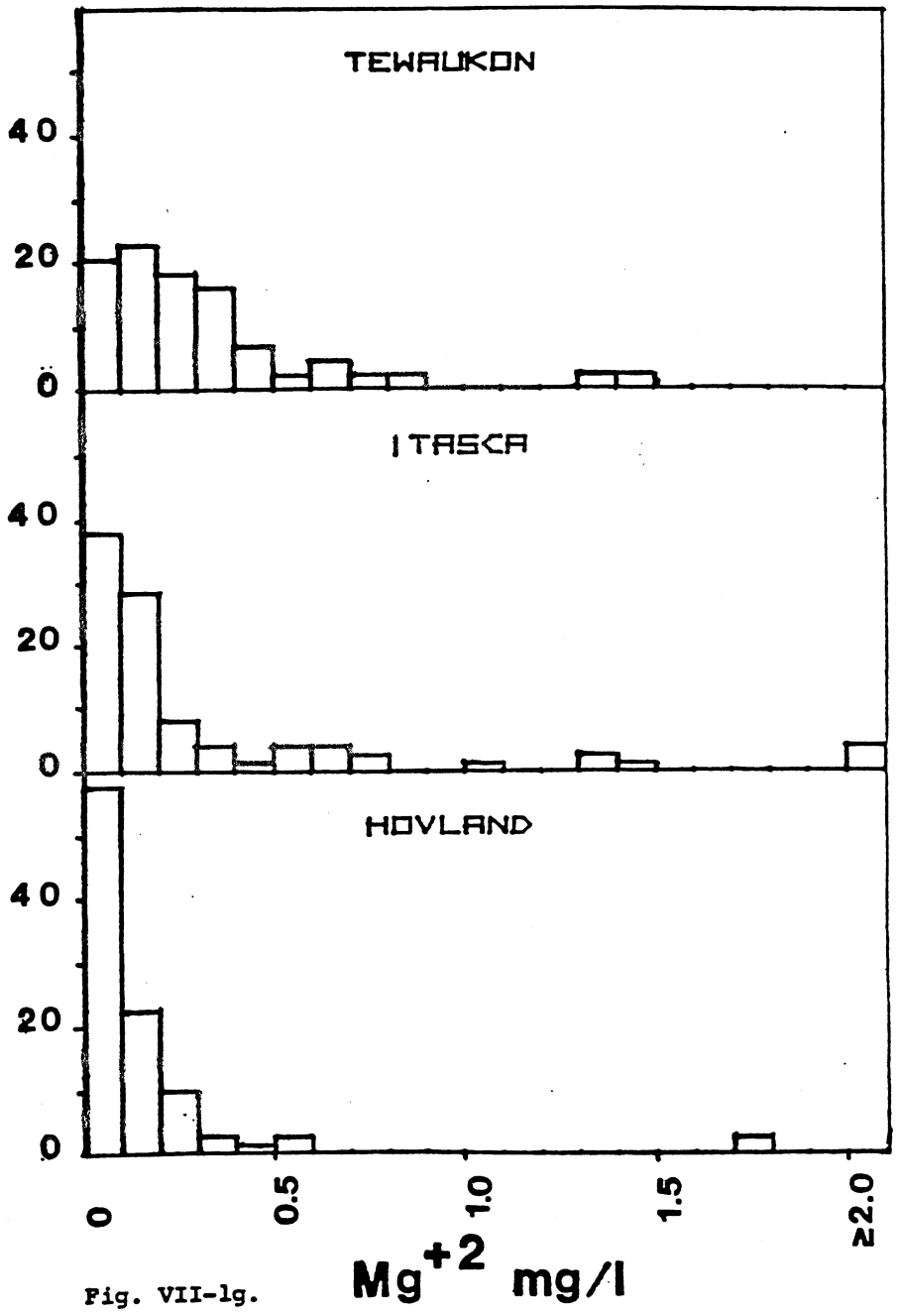

TEWAUKON
40
20
0
ITASCA
40
20
0
HOVLAND
40
20
0
0
0.5
1.0
1.5
≥2.0
Mg+2 mg/l

Fig. VII-1g.

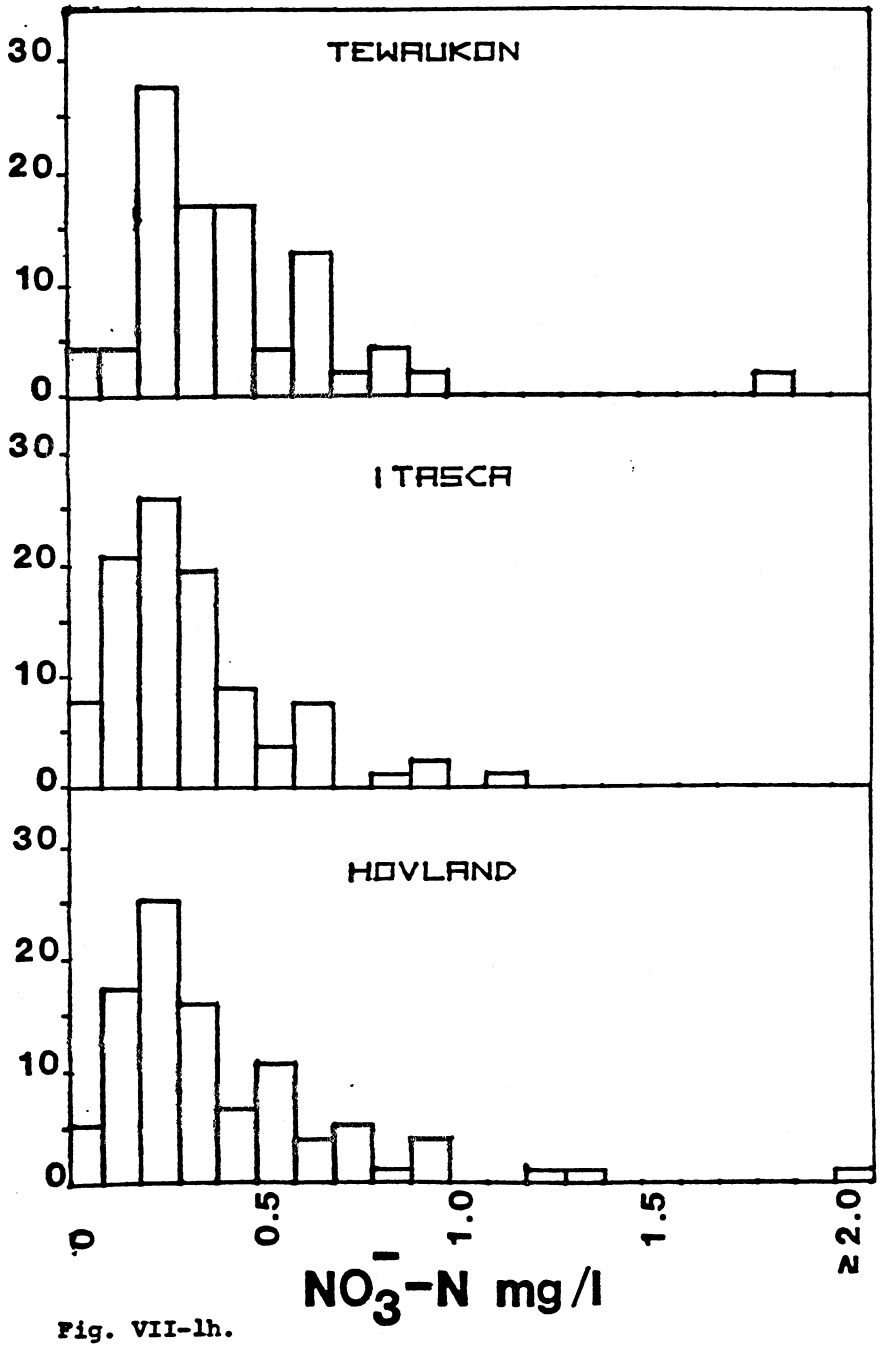


Fig. VII-1h.

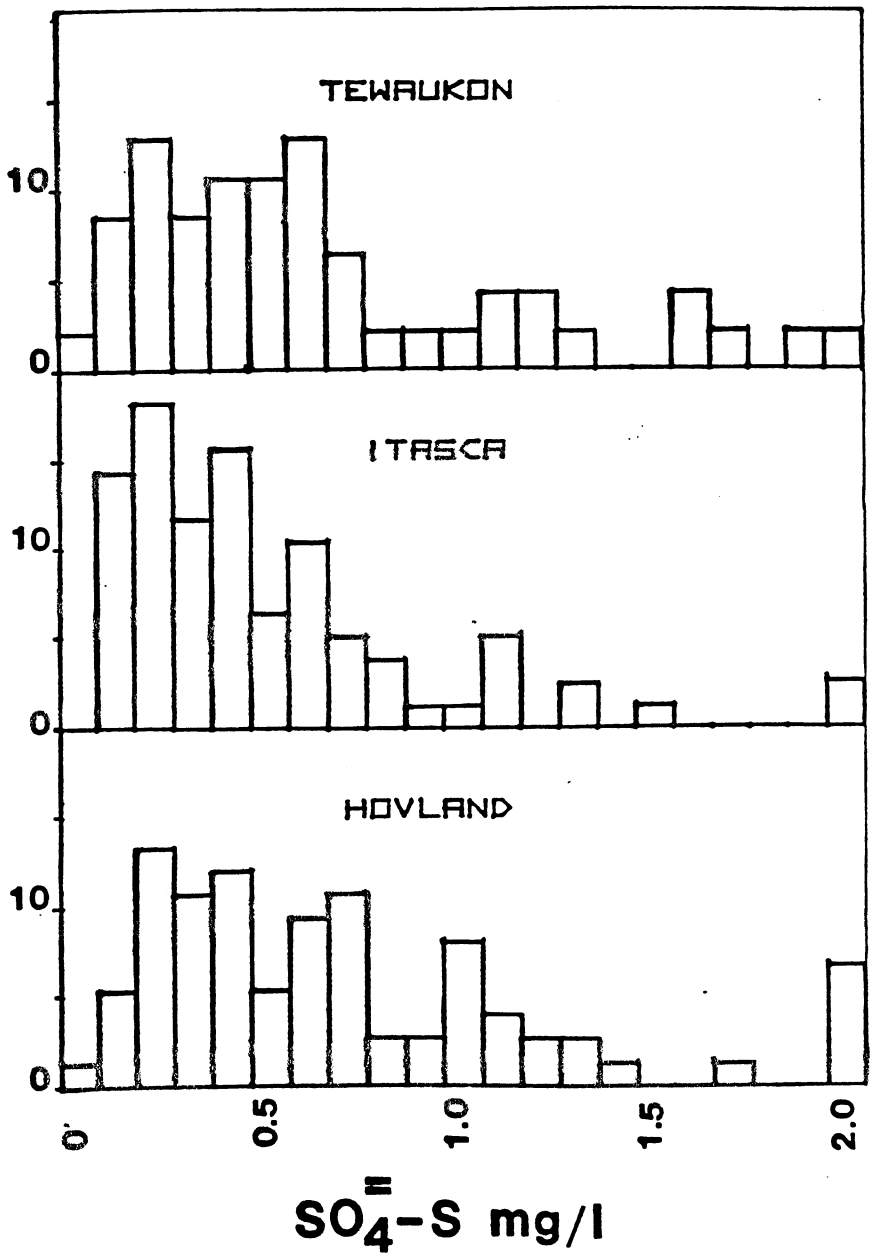


Fig. VII-1i.

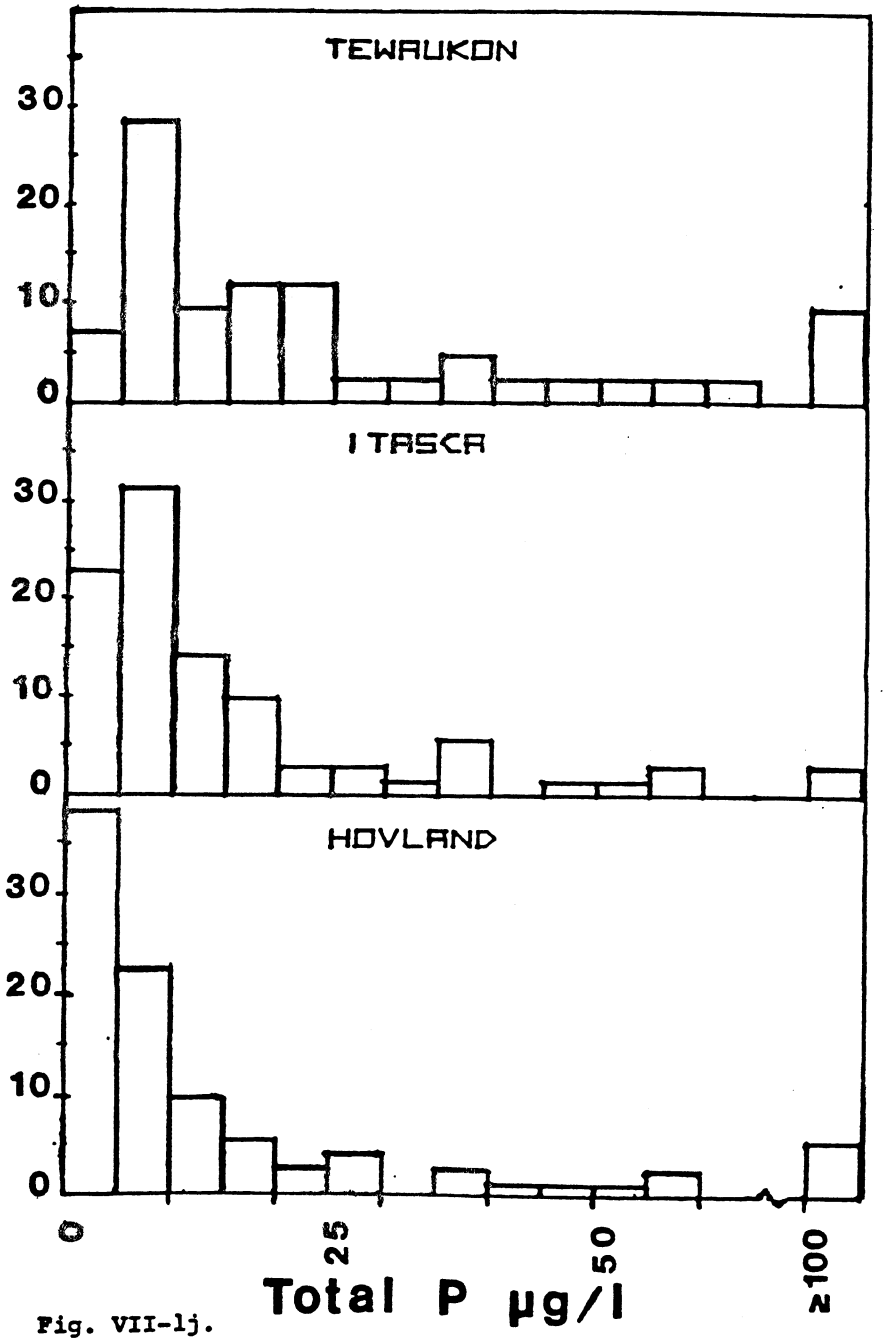

TEWAUKON
30
20
10
0
ITASCA
30
20
10
0
HOVLAND
30
20
10
0
0
25
50
≥100
Total P µg/l

Fig. VII-1j.

Appendix 8

Length of exposure and concentrations in samples of dry fallout that were not overly contaminated by bird feces. The presence of bird feces, pollen, or other organic material in the samples that were analyzed is indicated.

- indicates not analyzed

Collection Date	Days Exposed	Dissolution Volume	pH	Cond F	Na^+	K^+	NH_4	Ca^{++}	Mg^{++}	Cl^-	NO_3^-	$SO_4^=$	Alk	P_{tot}	Particulates >0.4 µm	% L.O.I.	Contamination
TEWAUKON																	
060978	52	500	7.86	91.6	-	-	10.7	-	-	-	-	-	-	>500	-	-	
071378	34	250	6.88	32.9	0.33	1.73	-	6.7	.99				-	>500	-	-	F(r)
042579	38	250	6.08	72.1	0.70	0.65	1.17	7.5	1.45	1.44	2.21	5.53	25	205	139	-	
051879	23	250	6.97	38.9	0.51	0.73	0.51	4.24	0.65	1.33	0.46	1.46	-	295	120	.23	
ITASCA																	
062078	60	50	6.48	53.9	-	-	4.91	1.21	-	-	-	-	426	>500	-	-	
070378	13	250	5.76	10.3	-	-	0.39	-	-	-	-	-	40.2	160	-	-	
072478	21	252	5.88	280	-	-	1.62	3.26	0.79	-	-	-	-	544	-	-	
081778	23	250	601	18.7	0.19	1.10	-	3.20	0.83	-	-	-	-	212	-	-	I
100478	49	250	660	39.2	0.61	3.45	-	2.74	0.59	1.06	0.57	1.42	-	510	21		P,I
110678	33	250	6.64	28.7	0.40	1.02	-	4.59	0.52	1.61	0.41	1.22	-	107	49	44	L (r)
123078	33	84*	4.90	62.	0.53	0.85	-	3.26	0.66	0.76	2.46	2.57	0	132	86.5	80	
020479	36	513*	4.43	22.2	0.16	0.12	0.15	-	0.07	0.51	0.68	0.32	0	14.5	4.8	-	
030979	33	580*	4.13	52.3	0.15	0.15	0.82	-	0.13	0.44	0.99	1.58	0	22.7	8.7	38	
040979	31	250	6.09	6.8	0.17	0.16	0.20	-	0.41	5.37	0.27	0.32	-	31	26	31	
051479	35	250	6.19	80.8	-	0.83	0.78	4.29	4.73	13	1.33	3.02	-	614	84	32	F(r)
061179	27	250	720	57.7	0.63	2.51	4.26	2.85	0.62	-	-	-	-	>1250	210	-	L,P F(r)
HOVLAND																	
042478	14	100	-	-	0.29	0.24	-	0.97	0.29	-	-	-	-	46	-	-	
050978	15	100	-	-	1.41	6.21	-	2.34	0.74	-	-	-	-	>500	-	-	F
060578	28	100	-	-	0.67	3.93	-	4.03	.91	-	-	-	-	>500	-	-	P
073178	28	250	6.93	60.8	-	-	-	-	-	-	-	-	-	-	-	-	F
082878	29	262	6.48	50.0	0.32	2.97	-	2.10	0.62	-	-	-	-	>1560			F(r)
103078	64	250	5.79	71.2	0.75	6.8	-	-	-	1.39	2.11	7.56	-	502	157	34	I(r)
112978	30	252	5.19	16.5	-	1.25	0.31	-	0.28	0.88	0.57	1.13	-	27	28	-	
050179	30	250	5.10	34.4	0.29	0.45	-	2.11	0.53	0.51	0.80	2.41	-	109	63	-	
060879	38	250	-	-	0.81	1.08	1.16	4.91	0.57	1.16	0.86	2.46	-	>500	-	-	P,M
070579	27	257	6.10	20.2	0.28	1.75	1.35	0.65	0.22	0.85	0.37	0.67	-	-	85	-	P,I, G

P Pollen
F Bird Feces
L Leaves -Plant fragments
S Seeds

M Miscellaneous Substances
I Insects
(r) removed before dissolution

* No H_2O added - volume of water present in collector due to light snow or resuspended snow

APPENDIX 9

MONTHLY CONCENTRATIONS

Figures IX-1a-i present the monthly volume-weighted mean concentrations for major ions and P_{tot}. Mean concentrations for the entire period are indicated along the right margin of each figure. Monthly wet-deposition estimates calculated from mean concentrations and volume are presented in Figs. IX-2a-i. The concentration of Na^+ at Itasca (Fig. IX-1b) during February and May 1979 was calculated without including two samples that had abnormally high Na^+ concentrations (> 5 mg ℓ^{-1}).

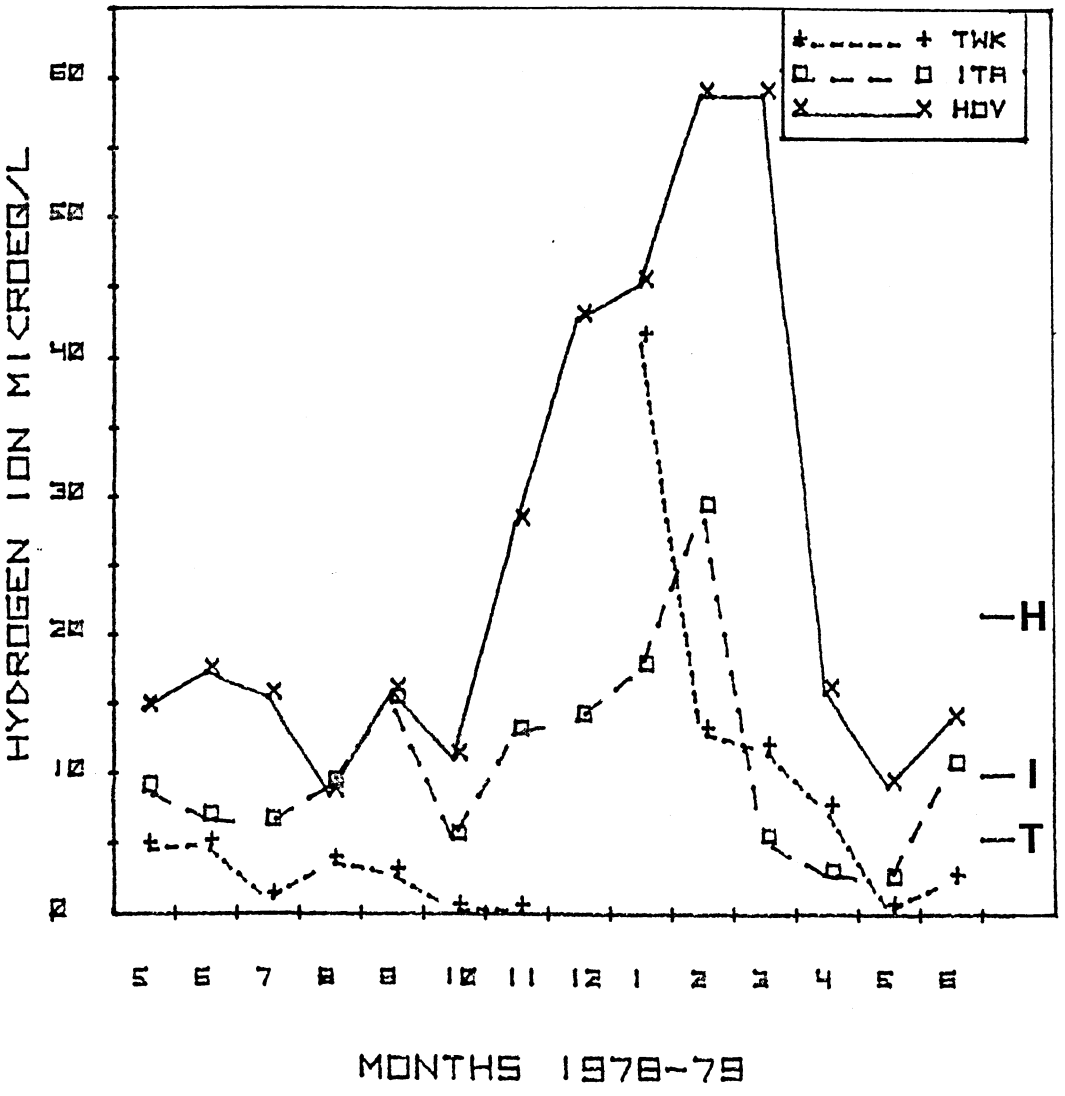

TWK
ITA
HOV
HYDROGEN ION MICROEQ/L
0
10
20
30
40
50
60
5
6
7
8
9
10
11
12
1
2
3
4
5
6
MONTHS 1978-79
H
I
T

Fig. IX-1a.

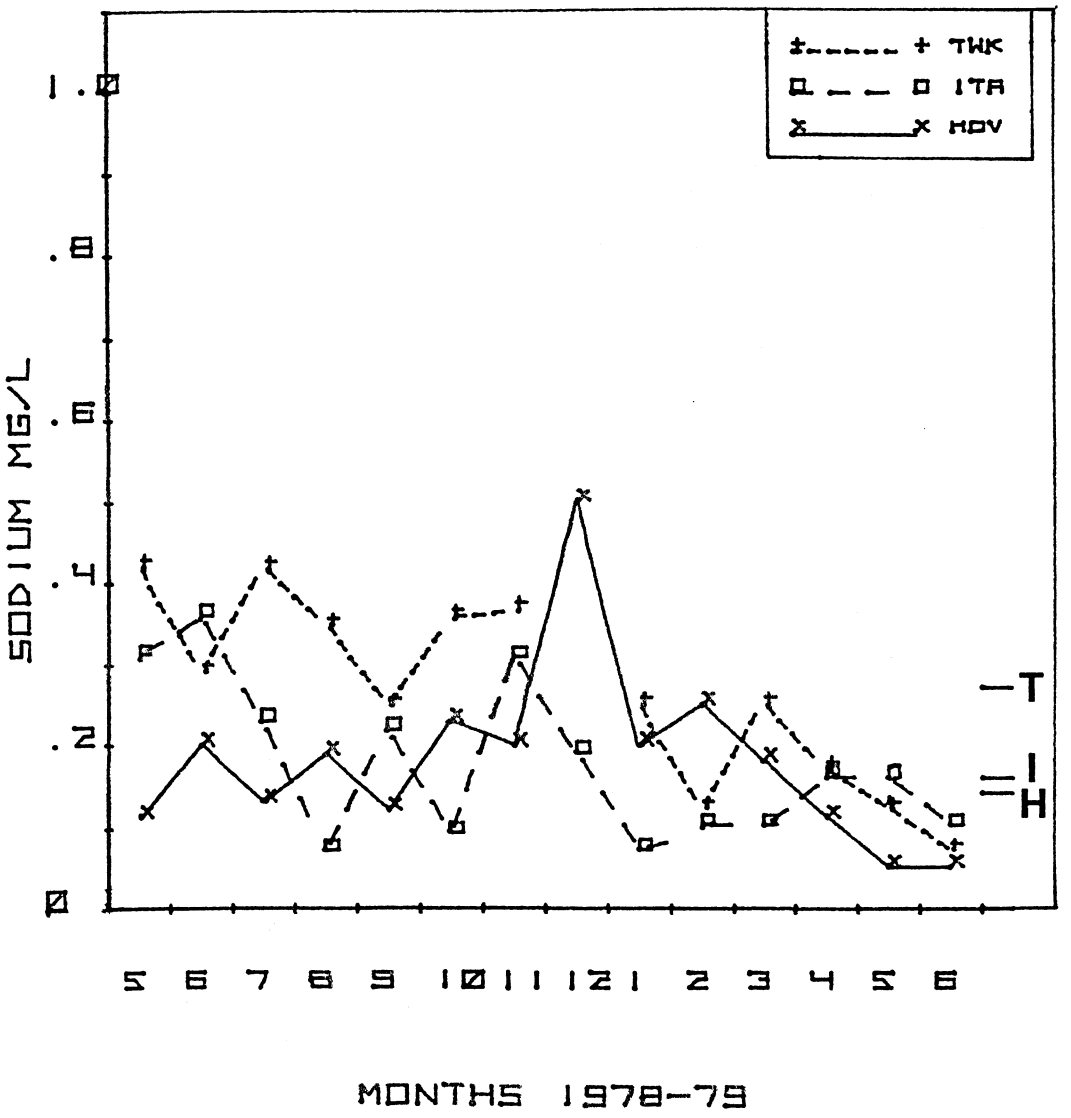

TWK
ITA
HOV
1.0
.8
.6
.4
.2
0
SODIUM MG/L
5 6 7 8 9 10 11 12 1 2 3 4 5 6
MONTHS 1978-79
T
I
H

Fig. IX-1b.

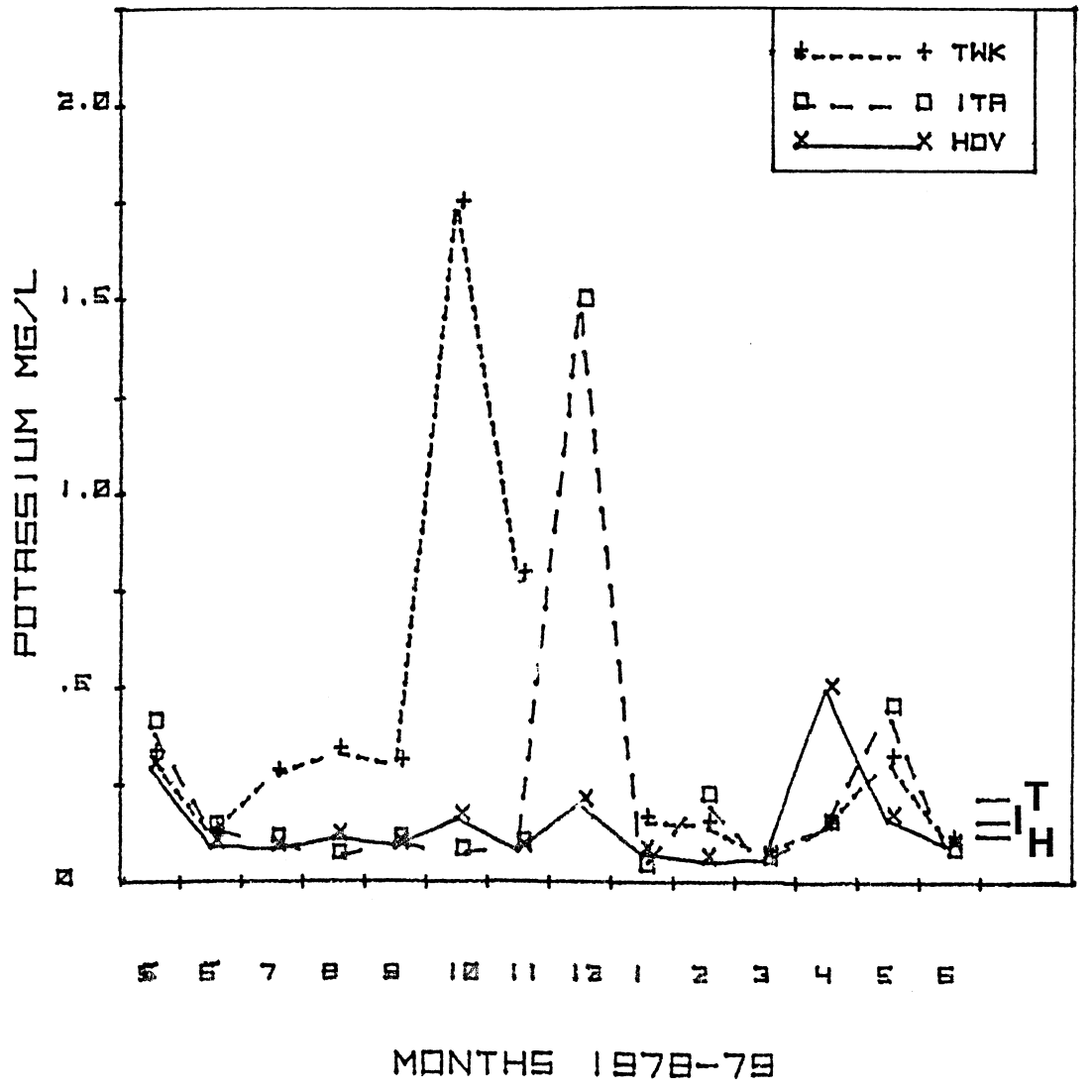

TWK
ITA
HDV
POTASSIUM MG/L
2.0
1.5
1.0
.5
0
5 6 7 8 9 10 11 12 1 2 3 4 5 6
MONTHS 1978-79

Fig. IX-1c.

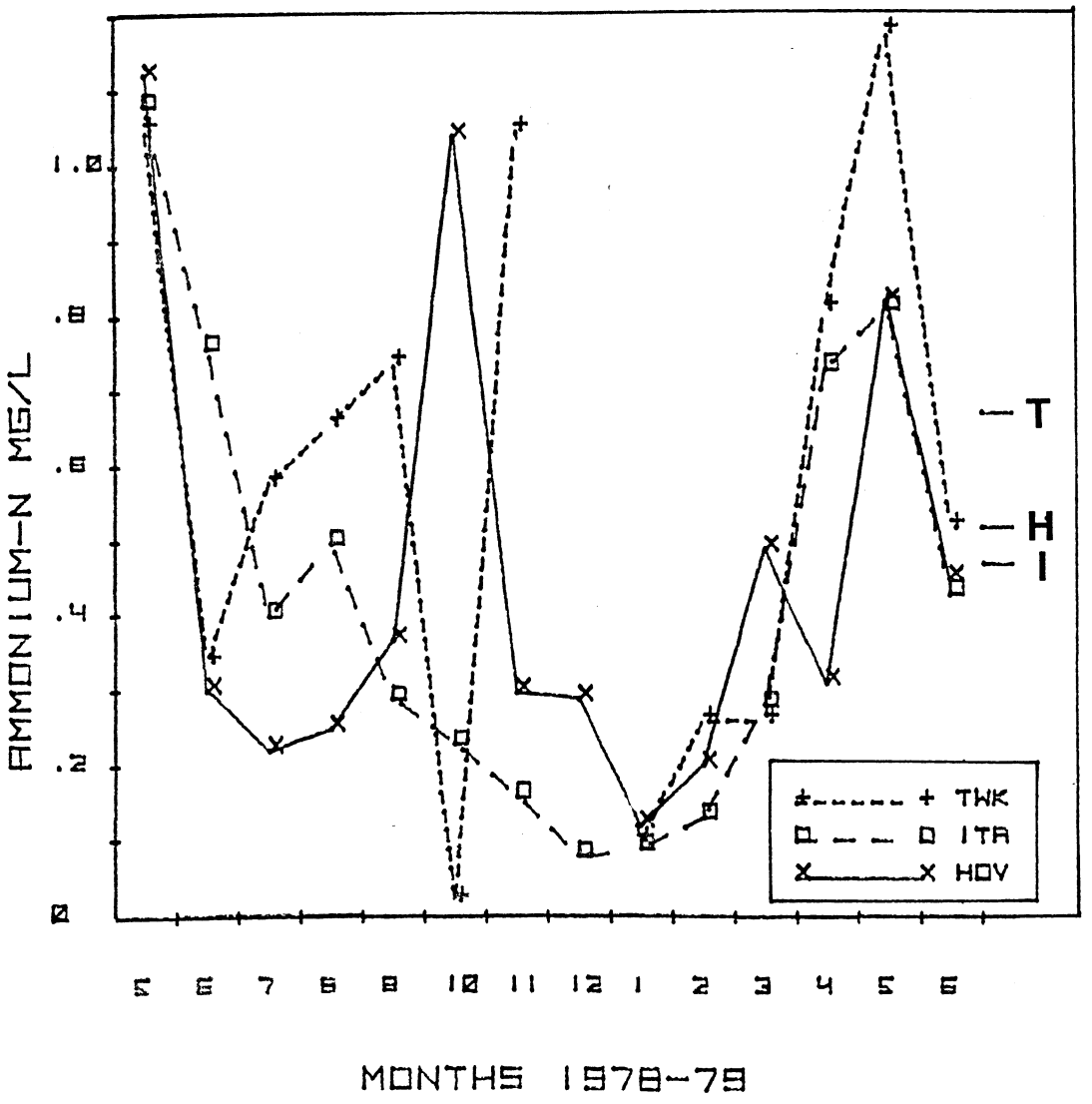

AMMONIUM-N MG/L
1.0
.8
.6
.4
.2
0
5
6
7
8
9
10
11
12
1
2
3
4
5
6
MONTHS 1978-79
T
H
I
TWK
ITA
HOV

Fig. IX-1d.

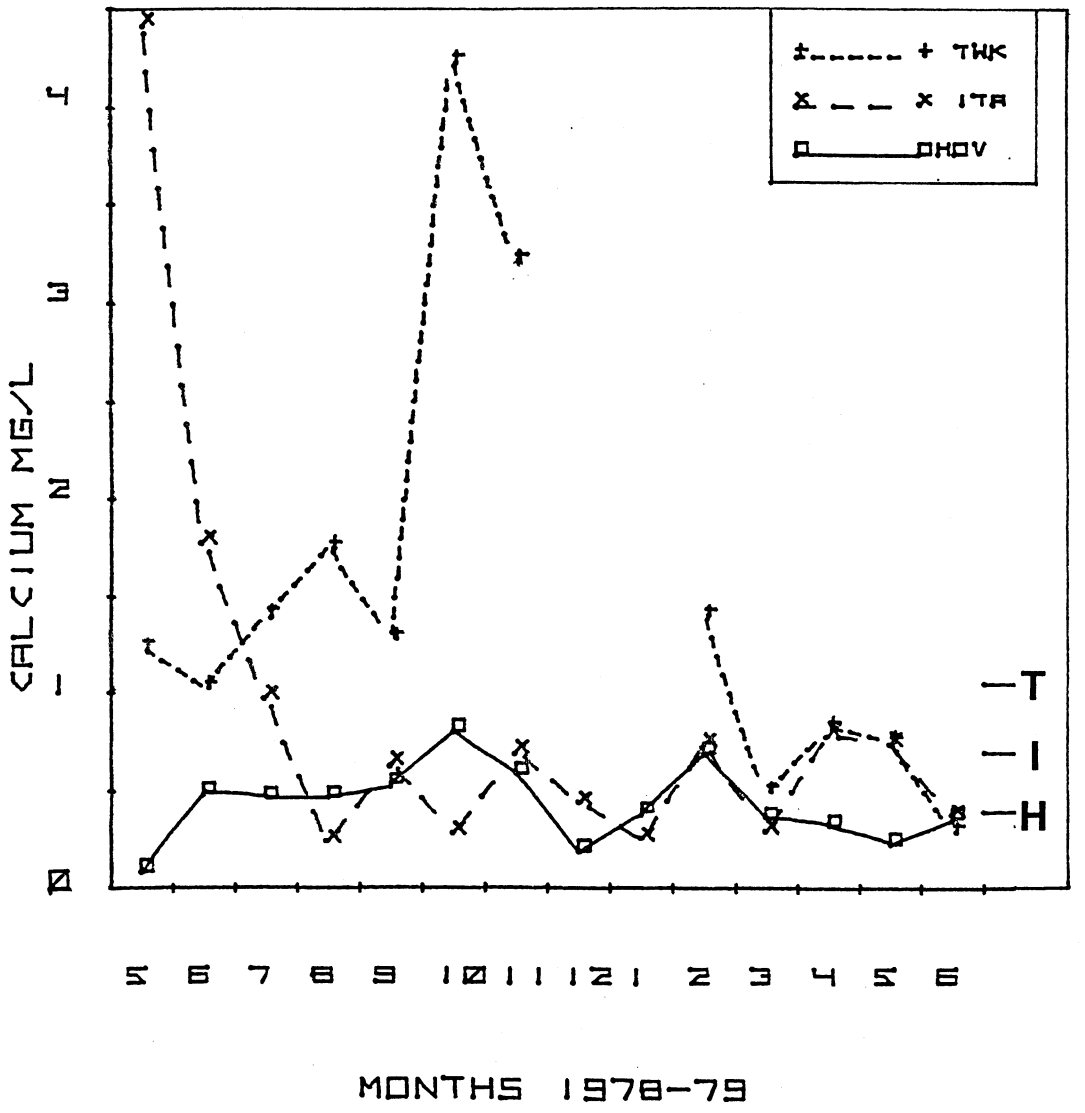


Fig. IX-1e.

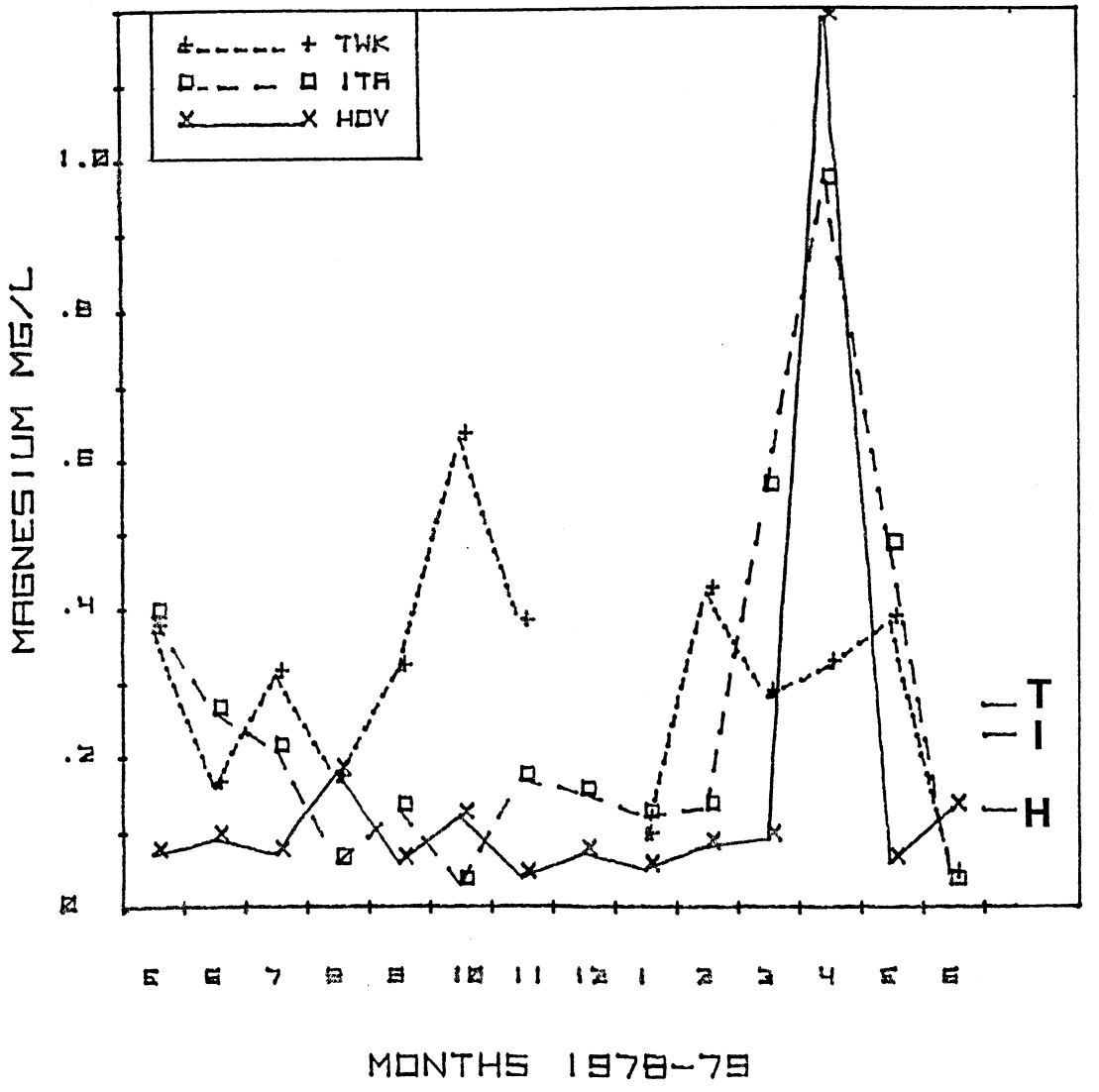


Fig. IX-1f.

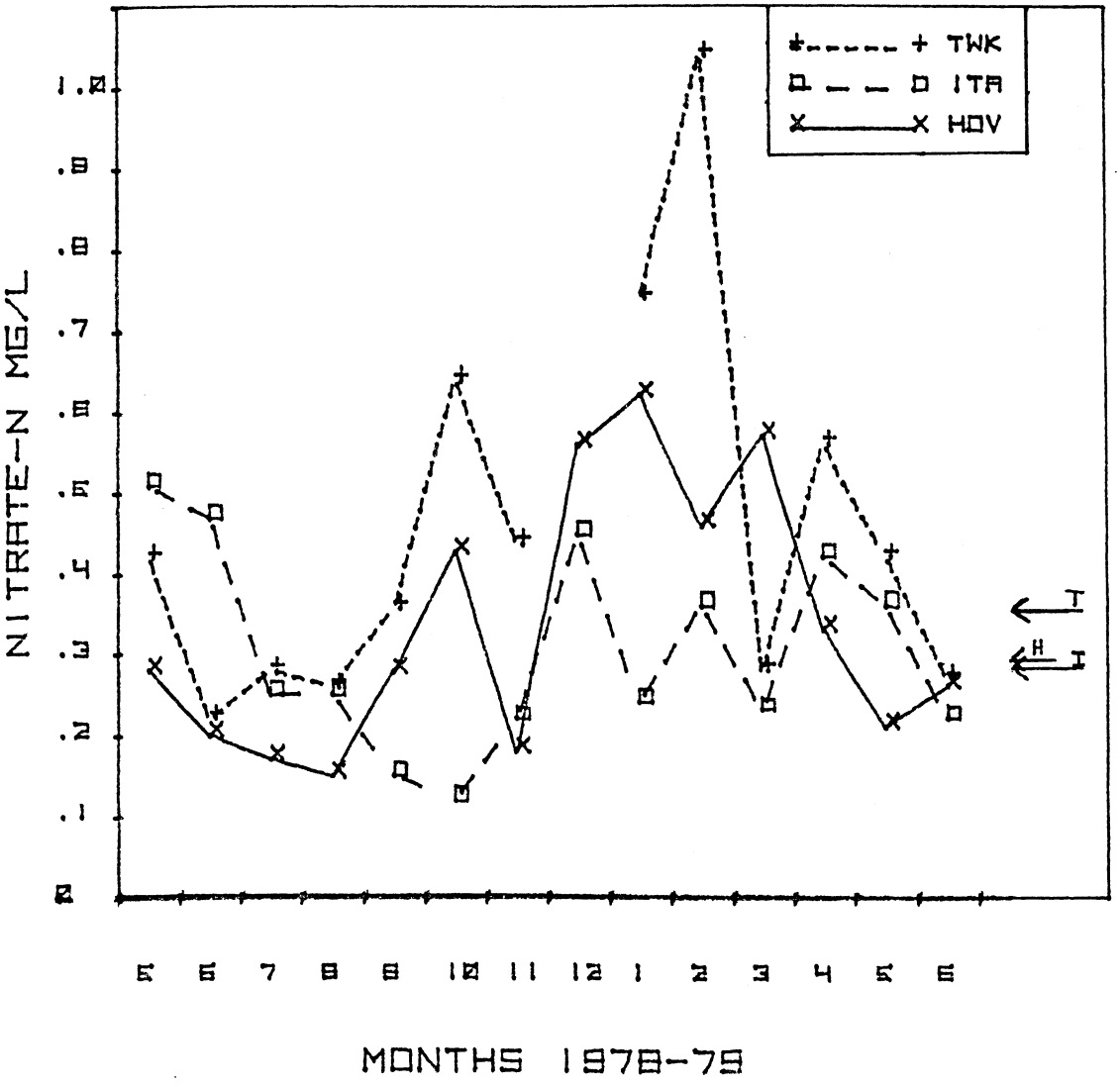

TWK
ITA
HOV
NITRATE-N MG/L
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
5 6 7 8 9 10 11 12 1 2 3 4 5 6
MONTHS 1978-79
T
H
H

Fig. IX-1g.

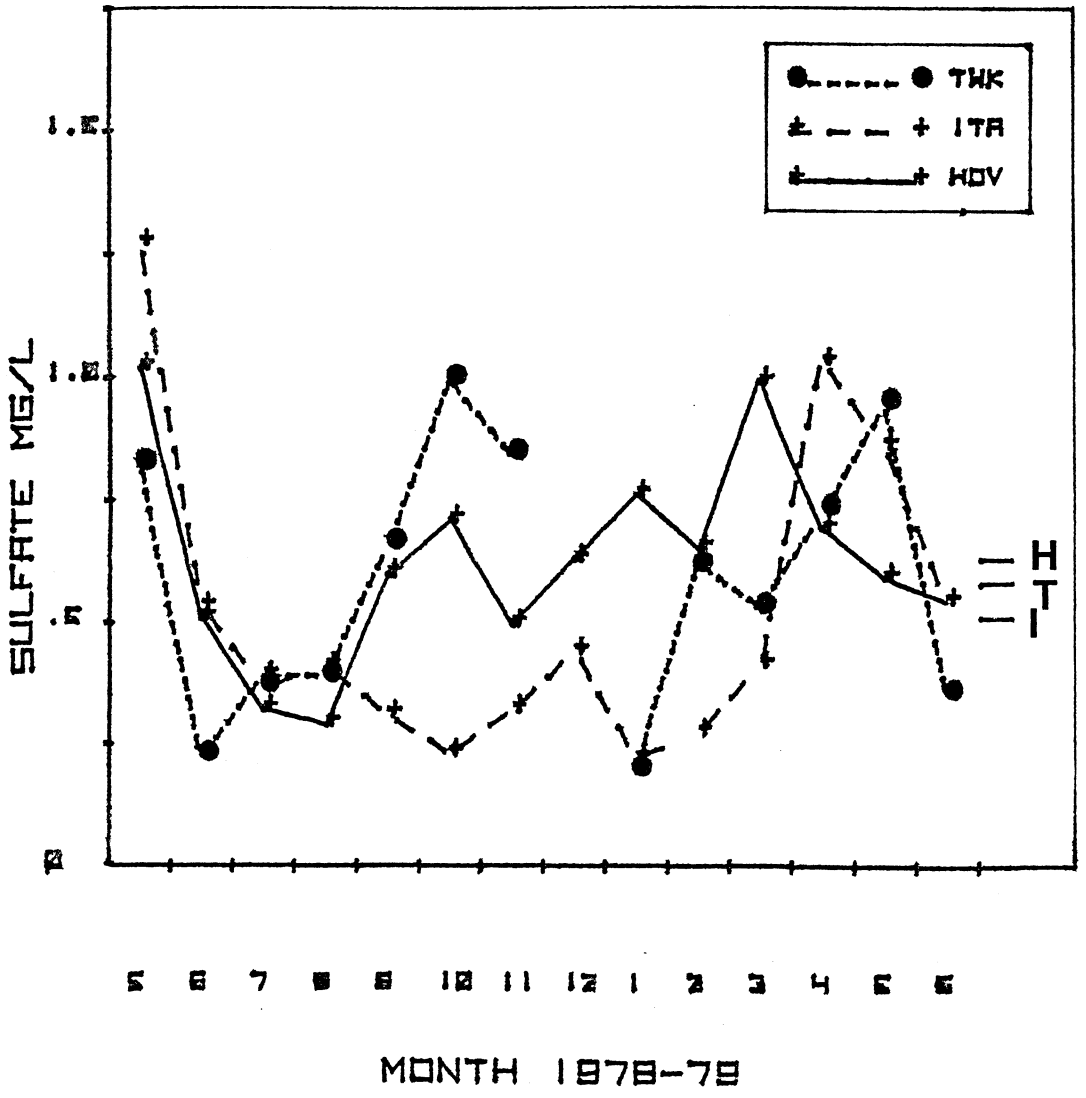


Fig. IX-1h.

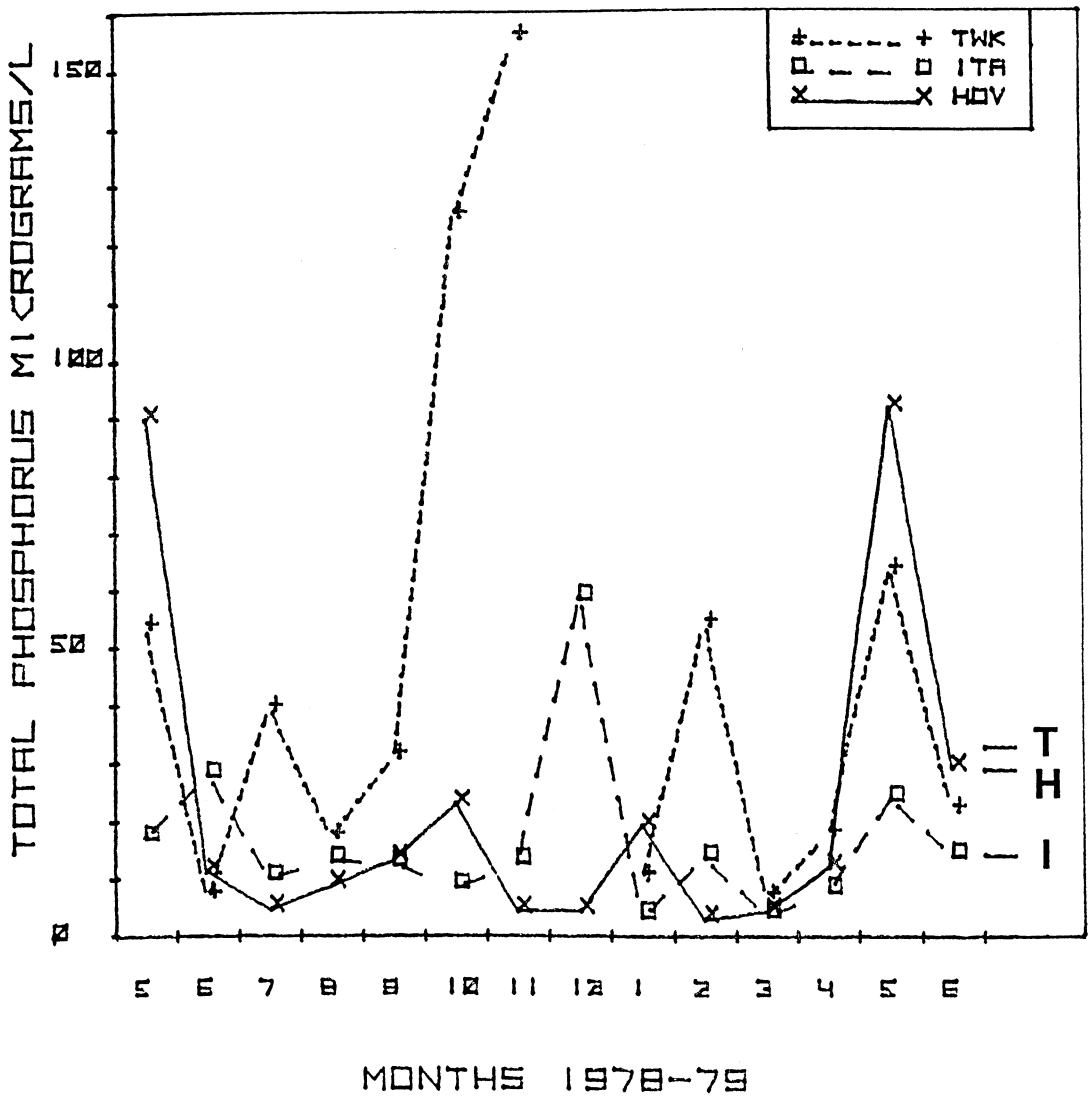

TOTAL PHOSPHORUS MICROGRAMS/L
150
100
50
0
TWK
ITA
HOV
THI
5 6 7 8 9 10 11 12 1 2 3 4 5 6
MONTHS 1978-79

Fig. IX-1i.

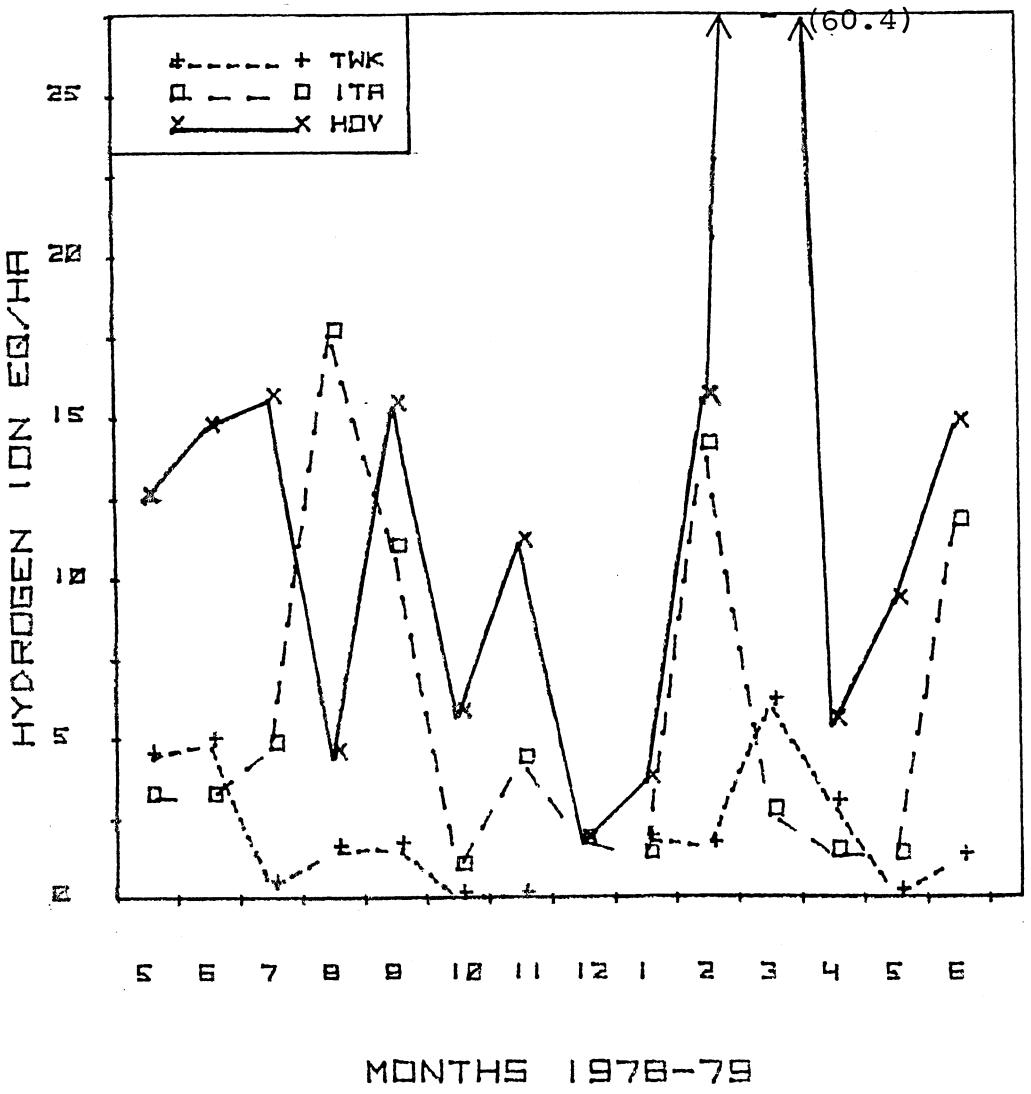

TWK
ITA
HOV
(60.4)
HYDROGEN ION EQ/HA
0
5
10
15
20
25
5 6 7 8 9 10 11 12 1 2 3 4 5 6
MONTHS 1978-79

Fig. IX-2a.

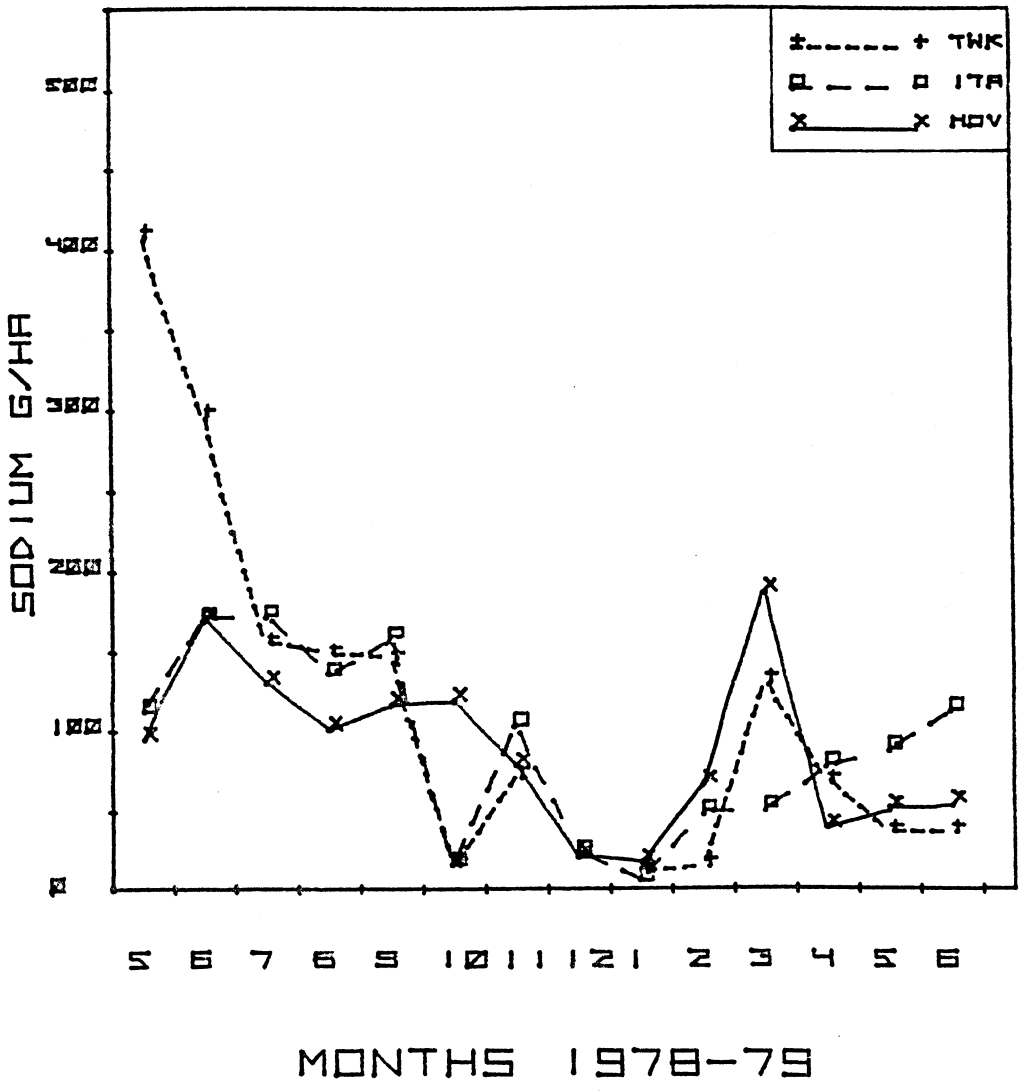

TWK
ITA
NOV
SODIUM G/HA
0
100
200
300
400
500
5 6 7 8 9 10 11 12 1 2 3 4 5 6
MONTHS 1978-79

Fig. IX-2b.

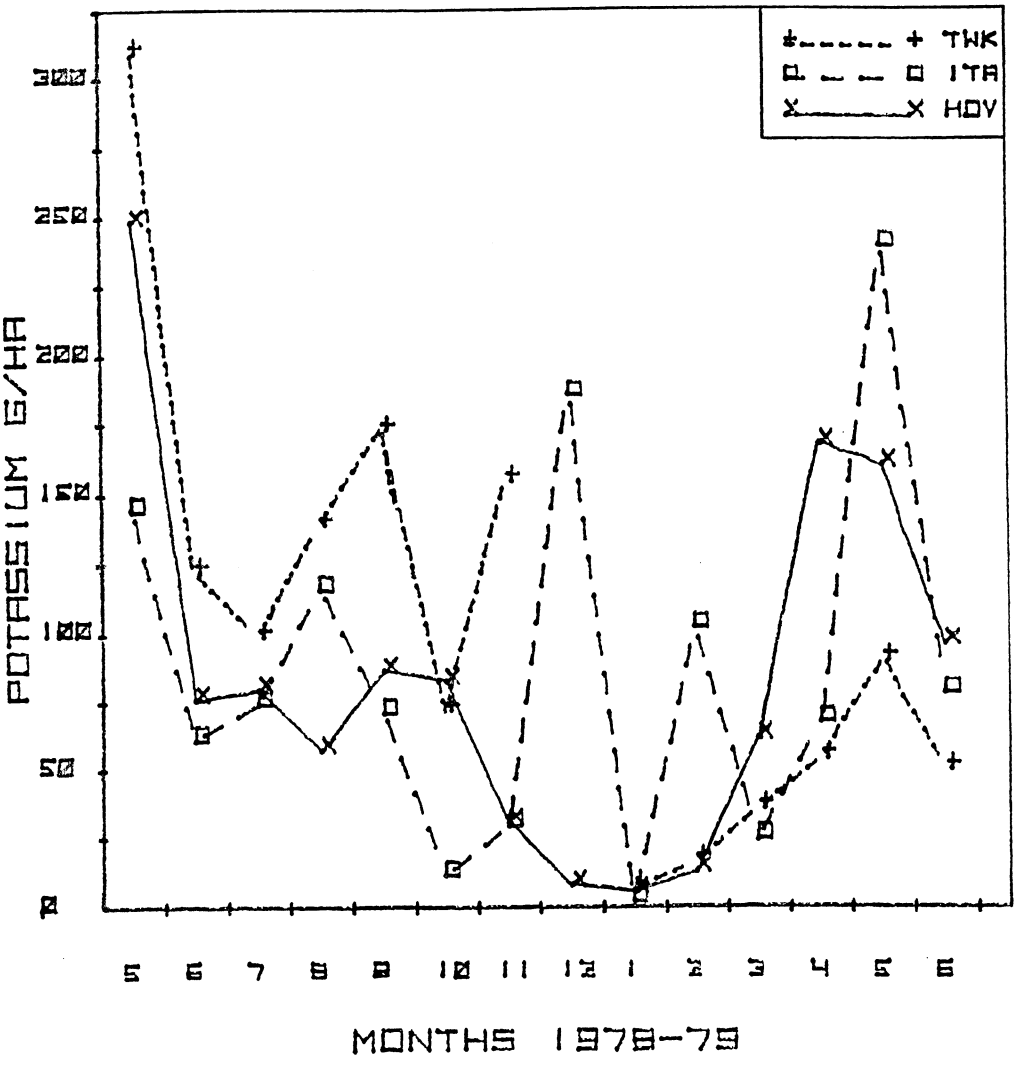

TWK
ITA
HOV
POTASSIUM G/HA
300
250
200
150
100
50
0
5
6
7
8
9
10
11
12
1
2
3
4
5
6
MONTHS 1978-79

Fig. IX-2c.

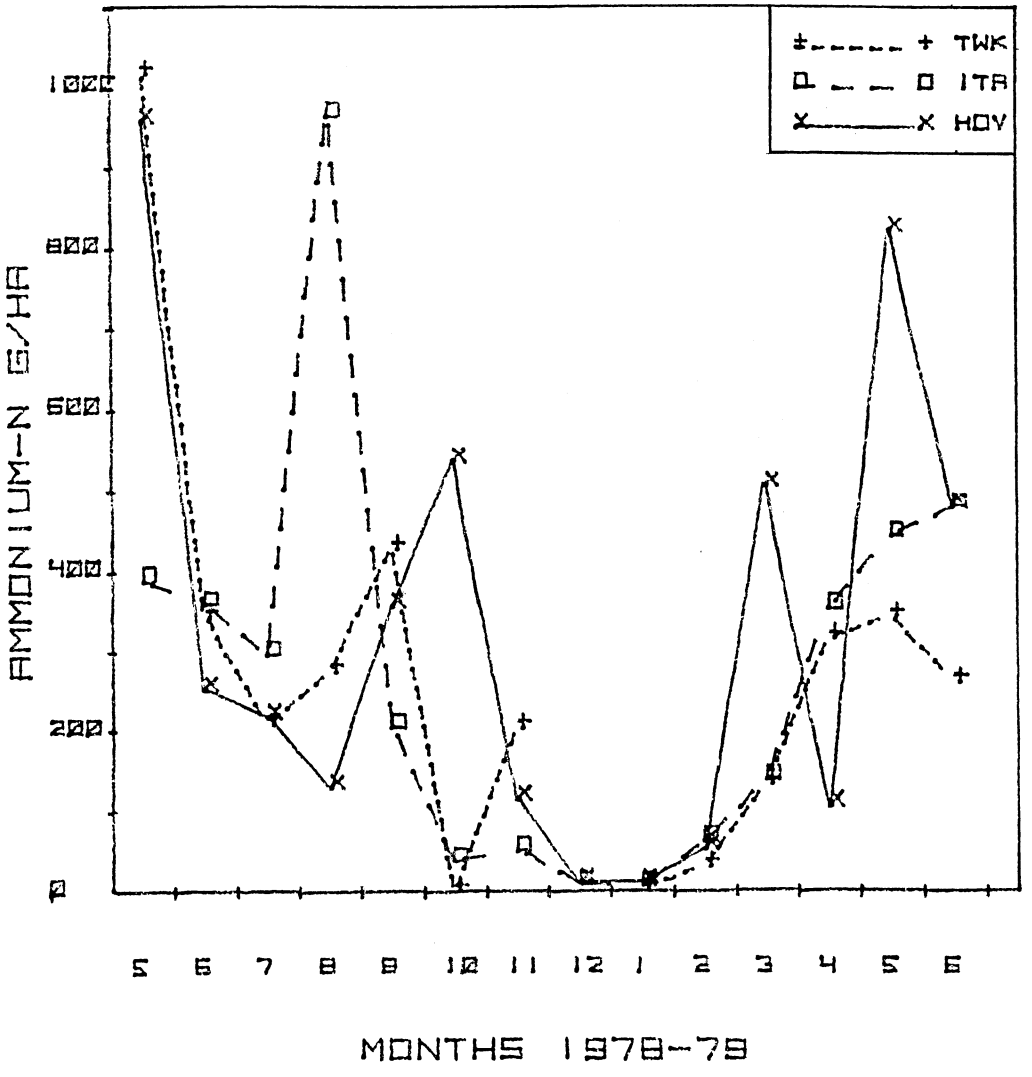

TWK
ITR
HOV
AMMONIUM-N G/HA
1000
800
600
400
200
0
5
6
7
8
9
10
11
12
1
2
3
4
5
6
MONTHS 1978-79

Fig. IX-2d.

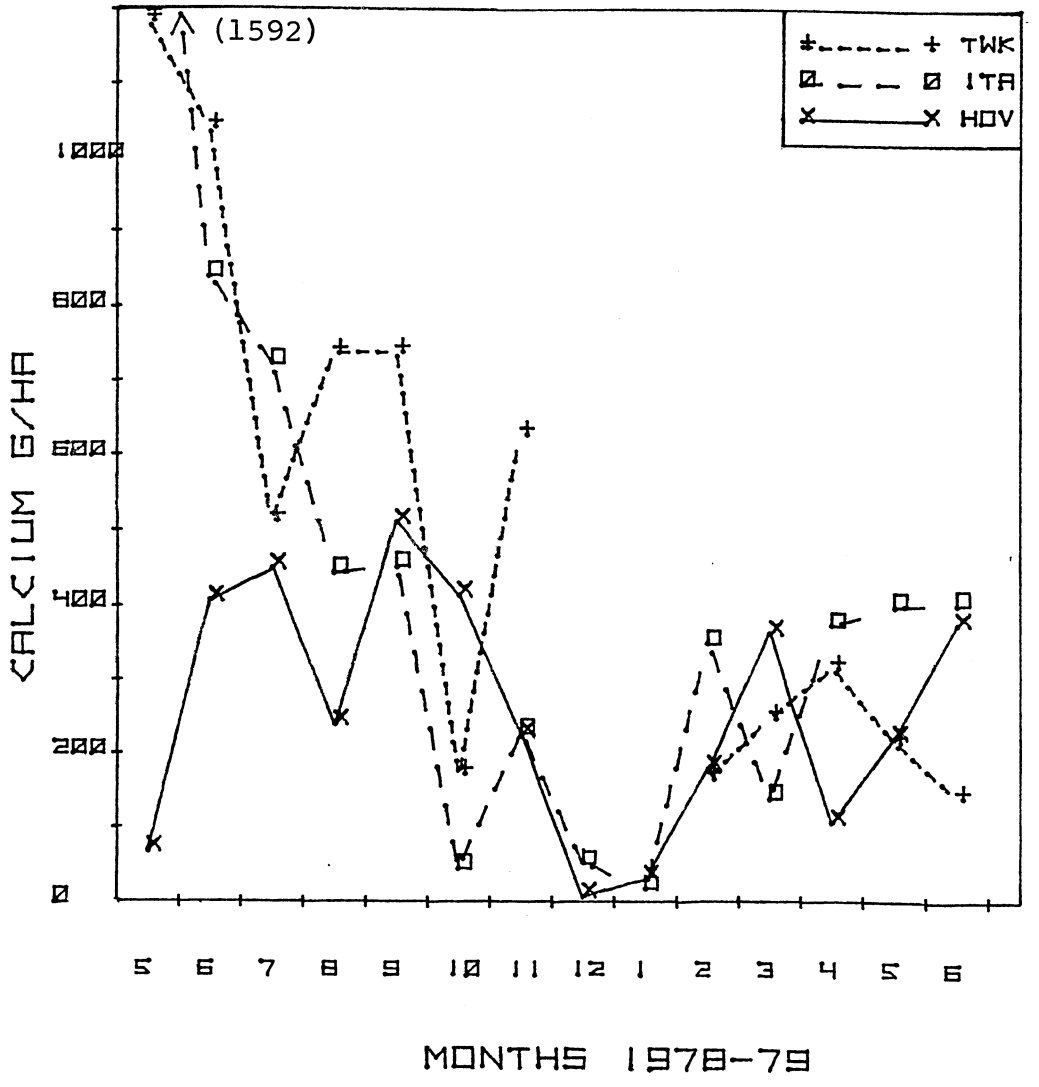

(1592)
TWK
ITA
HOV
CALCIUM G/HA
1000
800
600
400
200
0
5
6
7
8
9
10
11
12
1
2
3
4
5
6
MONTHS 1978-79

Fig. IX-2e.

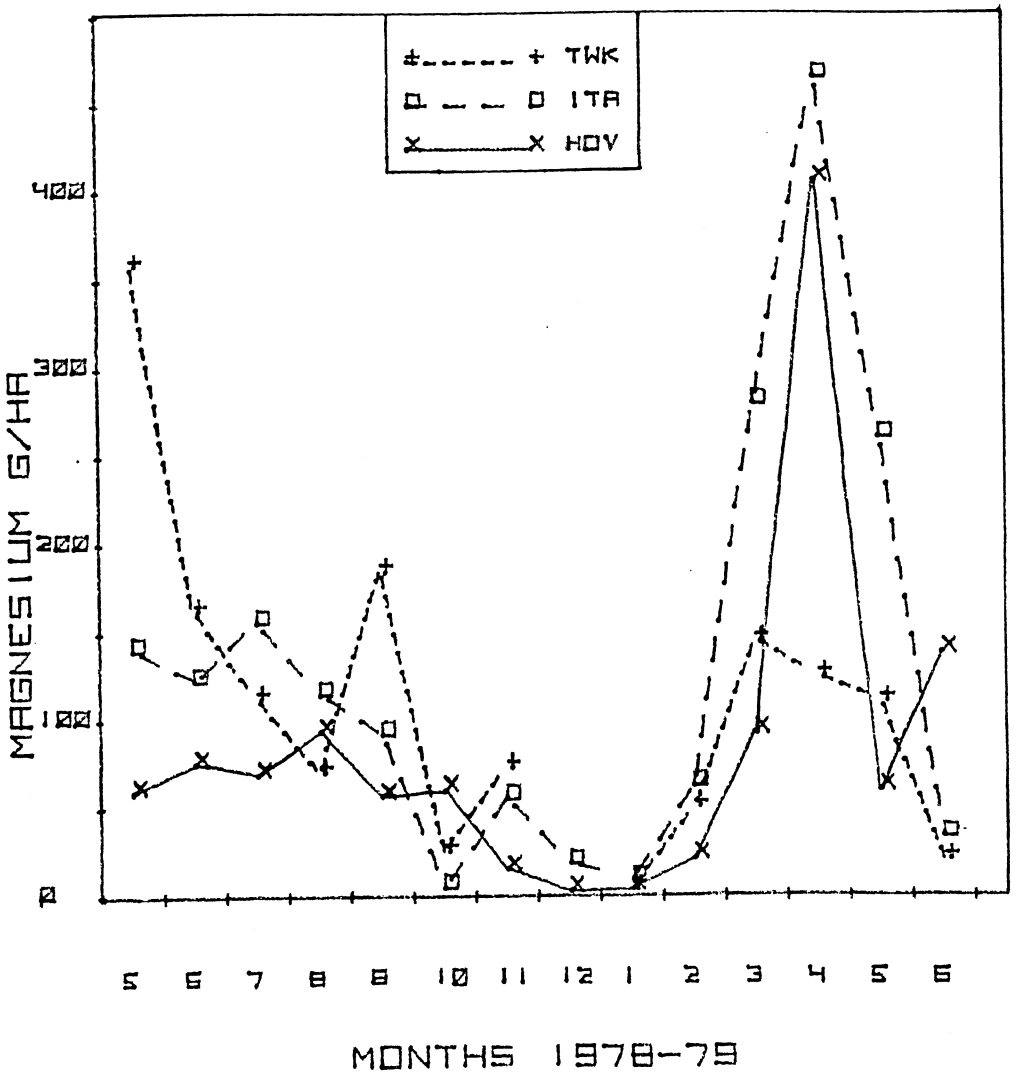

TWK
ITA
HOV
MAGNESIUM G/HA
400
300
200
100
0
5
6
7
8
9
10
11
12
1
2
3
4
5
6
MONTHS 1978-79

Fig. IX-2f.

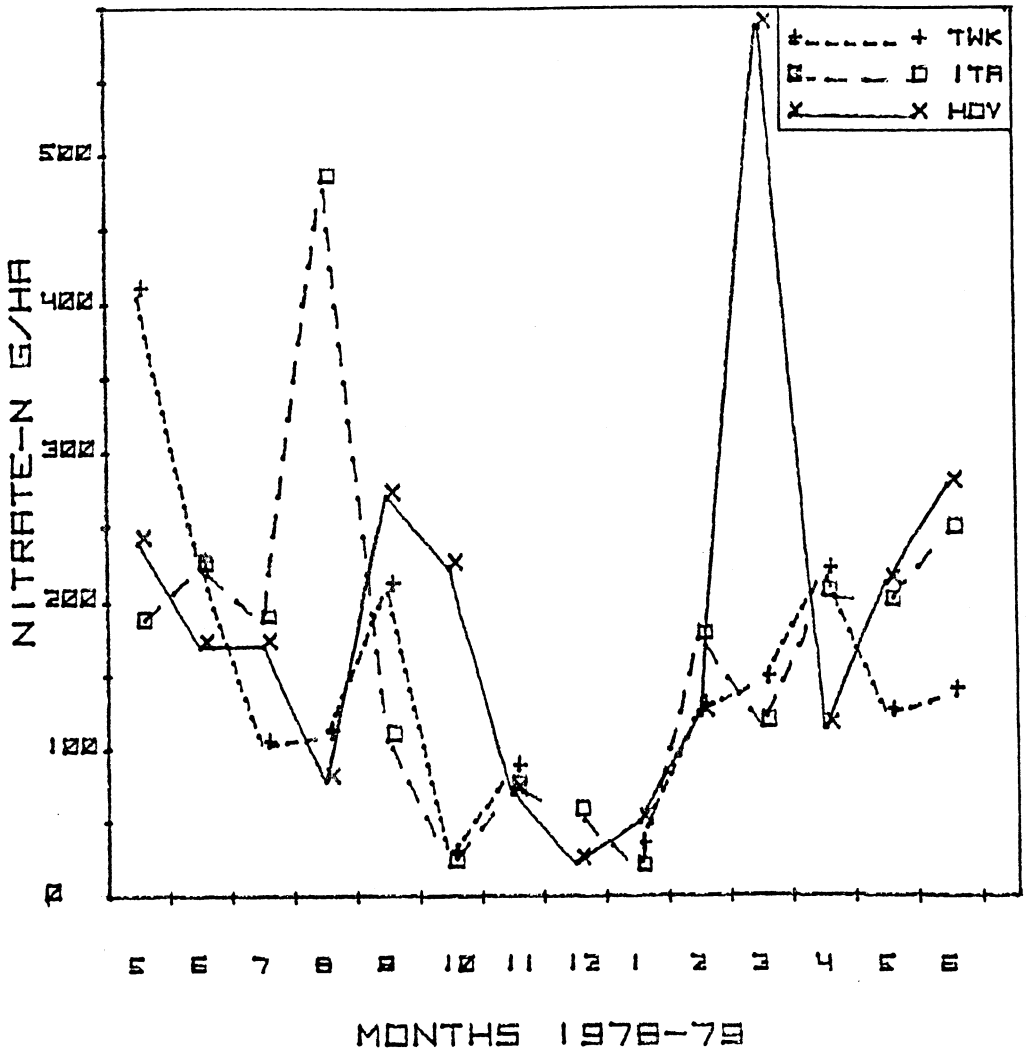

TWK
ITA
HOV
NITRATE-N G/HA
0
100
200
300
400
500
5
6
7
8
9
10
11
12
1
2
3
4
5
6
MONTHS 1978-79

Fig. IX-2g.

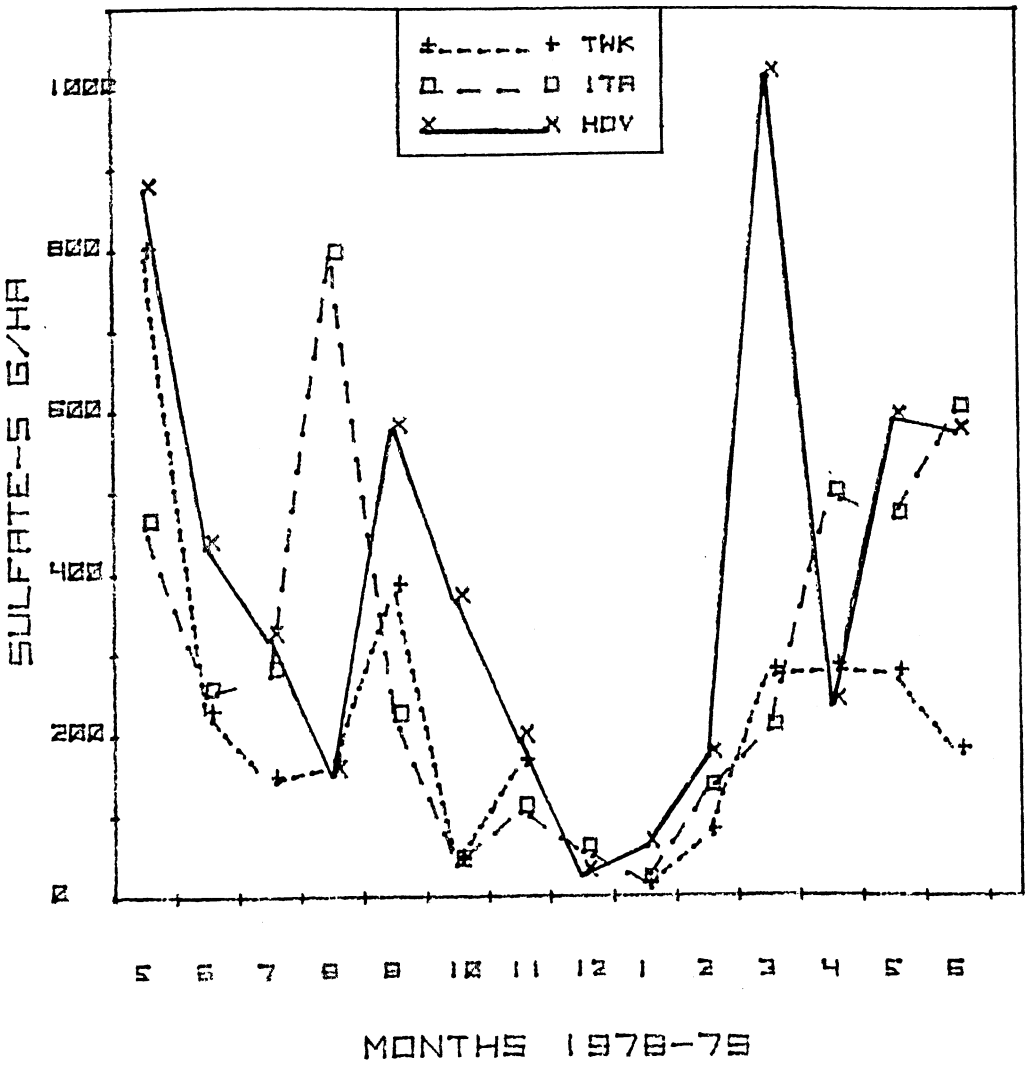

TWK
ITA
HOV
SULFATE-S G/HA
1000
800
600
400
200
0
5
6
7
8
9
10
11
12
1
2
3
4
5
6
MONTHS 1978-79

Fig. IX-2h.

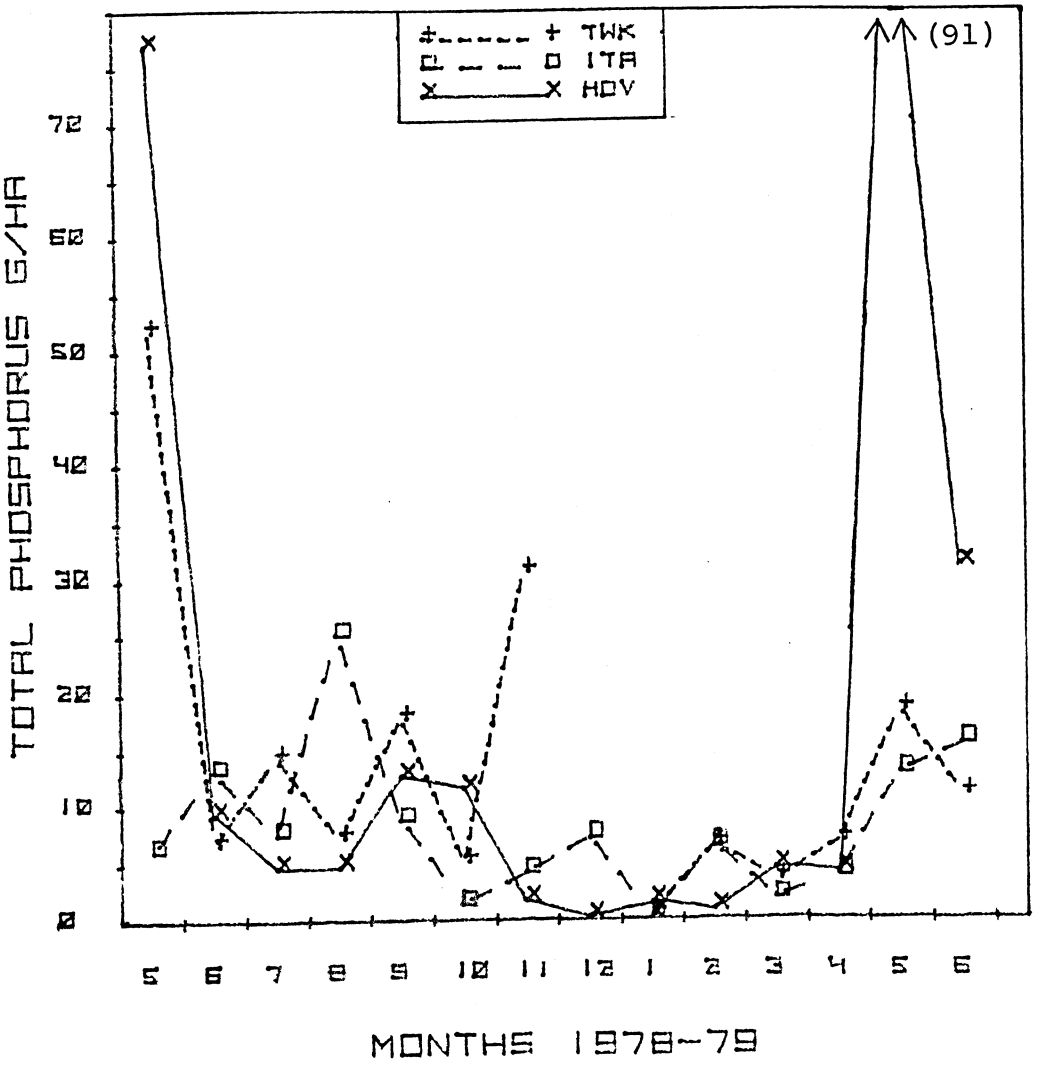

TWK
ITA
HDV
(91)
TOTAL PHOSPHORUS G/HA
0
10
20
30
40
50
60
70
5
6
7
8
9
10
11
12
1
2
3
4
5
6
MONTHS 1978-79

Fig. IX-2i

APPENDIX 10

Variable names, explanation of data codes, and raw data for snow samples collected in northeastern Minnesota during mid-March 1978, and along a belt transect from Tewaukon to Hovland during the winter of 1978-79. Table 1 has the March 1978 data, Table 2 the 1978-79 data.

HEADING	MEANING
TIME	Time of sampling 1 = Early winter--November-December 2 = Mid winter--January 3 = Late winter--March
SITE	Location of sampling, see Fig. 1 and Appendix 1, Fig. I-1 and Tables I-1 and I-2
TYPE	Type of sample collected 10 = Vertical core collected over polyethylene sheet 11 = Vertical core over natural surface 20 = Fresh surface horizon 21 = Bottom horizon 22 = Intermediate horizon 23 = Crust horizon from within snow pack 13 = Wet slush just above polyethylene sheet
AREA	Surface area of core in cm^2 (applies only to vertical cores)
MASS	Mass of sample in g, corresponds to volume in ml
PART	Particulates >0.4 µm in $mg\,\ell^{-1}$ dry weight
LOSSIG	% loss on ignition by particulates at 500°C
COND	Specific conductivity at 25°C µS
PH	pH
NA	Na^+ $mg\,\ell^{-1}$
K	K^+ "
NH4N	NH_4^+-N "
CA	Ca^{++} "
MG	Mg^{++} "
CL	Cl^- "
NO3N	NO_3^--N "
SO4S	$SO_4^=$-S "
TP	Total P $\mu g\,\ell^{-1}$
ALK	Alkalinity µeq l^{-1} (measured by Gran Titration)*

-0 indicates missing data

* March 1978 samples were not analyzed for Alkalinity because the pH was <5.5 in all cases (Alk = 0)

Table 1.

	TIME	SITE	TYPE	AREA	MASS	PART	LOSSIG
1	3.	34.	21.	192.0	395.	3.00	67.00
2	3.	34.	22.	-0	369.	1.00	-0
3	3.	34.	22.	-0	392.	12.00	83.00
4	3.	34.	11.	38.5	492.	5.00	40.00
5	3.	34.	20.	-0	303.	4.00	50.00
6	3.	34.	22.	-0	293.	4.00	-0
7	3.	34.	22.	-0	398.	1.00	0
8	3.	34.	21.	-0	567.	5.00	0
9	3.	33.	20.	-0	458.	4.00	25.00
10	3.	33.	22.	-0	393.	5.00	60.00
11	3.	33.	21.	-0	508.	15.00	40.00
12	3.	33.	11.	38.5	428.	-0	-0
13	3.	31.	11.	38.5	461.	8.00	100.00
14	3.	31.	20.	-0	544.	4.00	100.00
15	3.	31.	22.	-0	380.	5.00	40.00
16	3.	31.	23.	-0	411.	4.00	67.00
17	3.	31.	21.	-0	426.	6.40	63.00
18	3.	32.	11.	38.5	529.	9.60	67.00
19	3.	32.	20.	-0	296.	5.30	75.00
20	3.	32.	22.	-0	372.	9.00	22.00
21	3.	32.	21.	-0	505.	12.00	33.00
22	3.	36.	11.	38.5	532.	12.00	47.00
23	3.	36.	20.	-0	308.	8.00	83.00
24	3.	36.	22.	-0	340.	13.00	80.00
25	3.	36.	22.	-0	397.	10.00	70.00
26	3.	36.	23.	-0	450.	34.00	26.00
27	3.	36.	21.	-0	573.	82.00	60.00
28	3.	36.	23.	-0	516.	38.00	26.00
29	3.	37.	11.	38.5	482.	10.00	-0
30	3.	37.	20.	-0	277.	0	-0
31	3.	37.	22.	-0	338.	6.70	80.00
32	3.	37.	23.	-0	469.	15.00	26.00
33	3.	37.	21.	-0	513.	4.00	80.00
34	3.	38.	11.	38.5	583.	4.80	67.00
35	3.	38.	20.	-0	292.	2.70	0
36	3.	38.	21.	-0	364.	-0	-0
37	3.	38.	21.	-0	584.	1.60	0
38	3.	39.	11.	38.5	626.	3.00	0
39	3.	39.	20.	-0	336.	5.00	-0
40	3.	39.	22.	-0	374.	32.00	76.00
41	3.	39.	23.	-0	446.	4.80	17.00
42	3.	39.	21.	-0	551.	.80	0

Table 1.

	COND	PH	NA	K	NH4N	CA	MG	CL	NO3N	SO4S	TP
1	9.6	4.76	.16	.13	.29	.08	.01	.22	.20	.29	5.10
2	19.4	4.67	.83	.25	.35	.26	.07	1.21	.46	.39	22.10
3	21.9	4.50	.42	.29	.56	.28	.03	.70	.58	.44	13.80
4	14.3	4.64	.22	.16	.25	.14	.02	.37	.34	.34	11.60
5	13.1	4.78	.13	.12	.36	1.14	.01	.20	.25	.42	5.60
6	17.9	4.54	.41	.27	.21	1.04	.02	1.38	.40	.32	11.10
7	22.4	4.41	.30	.14	.25	.16	.02	.41	.53	.40	9.70
8	11.0	4.83	.25	.35	.26	.69	.02	.41	.19	.28	3.70
9	9.3	4.82	.23	.10	.21	.10	.01	.73	.17	.13	4.90
10	17.3	4.42	.12	.08	.09	.16	.02	.21	.39	.30	3.40
11	12.1	4.68	.19	.14	.18	.22	.04	1.33	.21	.37	13.20
12	13.4	4.69	.13	.10	.11	.09	.02	.35	.27	.28	4.80
13	11.5	4.70	.19	.27	.18	.18	.03	.27	.23	.26	9.10
14	5.3	5.03	.08	.07	.09	.07	.04	.36	.10	.09	1.30
15	13.1	4.69	.07	.05	.07	.10	.01	.15	.27	.24	4.30
16	14.7	4.55	.19	.07	.03	.08	.01	.21	.39	.19	7.70
17	7.2	5.01	.08	.17	.09	.11	.02	.07	.14	.20	14.30
18	10.6	4.73	.09	-0	.11	.11	.02	.09	.22	.18	11.30
19	8.8	4.82	.10	.06	.09	.06	.60	.23	.20	.18	3.30
20	13.2	4.60	.14	.12	.08	.17	.01	.19	.34	.21	11.40
21	6.9	4.99	.08	.10	.05	.29	.05	.18	.18	.15	10.20
22	10.8	4.77	.11	.11	.03	.13	.04	.18	.22	.23	29.40
23	7.8	4.89	.39	.13	.08	.09	.01	.15	.15	.15	1.80
24	13.1	4.54	.11	.11	.03	.05	.01	.27	.30	.16	9.70
25	12.2	4.61	.10	.11	.10	.06	.03	.13	.25	.18	14.20
26	18.3	4.49	.14	.14	.18	.23	.04	.22	.38	.42	27.90
27	7.5	5.03	-0	-0	-0	.23	.04	.24	.19	.29	45.30
28	9.1	4.96	.16	.22	.27	.31	.10	.16	.20	.30	21.50
29	9.5	4.76	.16	.26	.10	.15	.03	.36	.20	.36	5.80
30	6.2	5.03	.15	.14	.12	.06	.02	2.44	.13	.31	3.20
31	14.0	4.55	.33	.12	.03	.55	.02	.16	.32	.14	7.20
32	8.9	4.90	.09	.10	.08	.36	.08	.08	.19	.28	11.40
33	9.8	4.72	.17	.06	.03	.62	.02	.43	.29	.13	1.20
34	12.8	4.72	.19	.16	.26	.20	.04	.22	.23	.32	8.00
35	6.0	4.96	.10	.08	.09	.06	.00	.03	.11	.08	1.20
36	7.0	4.89	.12	.14	.05	.58	.04	.30	.16	.17	3.70
37	7.0	5.02	.06	.09	.17	.17	.03	.10	.21	.28	9.20
38	10.8	4.72	.09	.11	.04	.30	.02	.14	.22	.24	8.20
39	7.9	4.86	.08	.16	.06	.02	.01	.16	.13	.13	1.50
40	9.9	4.75	.07	.08	.01	.08	.00	.07	.24	.13	12.00
41	12.4	4.69	.05	.05	.07	.14	.04	.05	.22	.39	6.20
42	7.4	5.01	.07	.07	.17	.11	.02	.93	.20	.14	6.40

Table 2.

	TIME	SITE	TYPE	AREA	MASS	PART	LOSSIG	ALK
1	1.	25.	11.	192.0	338.	2.00	50.00	0
2	1.	24.	11.	192.0	260.	6.70	60.00	0
3	1.	24.	20.	-0	196.	2.70	0	0
4	1.	22.	11.	231.0	203.	4.00	67.00	0
5	1.	21.	11.	115.0	311.	3.00	0	0
6	1.	21.	20.	-0	282.	12.00	44.00	89.00
7	1.	10.	11.	192.0	236.	4.00	-0	7.50
8	1.	10.	20.	-0	-0	33.00	15.00	152.00
9	1.	35.	11.	77.0	339.	12.00	33.00	0
10	1.	30.	11.	77.0	403.	27.00	75.00	0
11	2.	20.	11.	77.0	420.	4.00	-0	0
12	2.	12.	11.	77.0	377.	17.00	14.00	-0
13	2.	12.	11.	77.0	377.	17.00	14.00	-0
14	2.	10.	10.	77.0	448.	76.00	15.00	-0
15	2.	10.	20.	-0	231.	42.00	36.00	-0
16	2.	10.	11.	77.0	401.	29.60	-0	-0
17	2.	11.	11.	38.5	500.	159.00	9.00	-0
18	2.	21.	10.	77.0	324.	12.00	67.00	0
19	2.	21.	20.	-0	334.	-0	-0	0
20	2.	21.	11.	115.0	442.	4.80	0	-0
21	2.	23.	11.	77.0	395.	8.80	-0	-0
22	2.	23.	11.	77.0	395.	8.80	-0	-0
23	2.	30.	10.	77.0	493.	4.00	40.00	0
24	2.	30.	10.	77.0	493.	4.00	40.00	0
25	2.	40.	10.	77.0	325.	0	-0	0
26	2.	32.	10.	38.5	295.	5.60	0	0
27	2.	41.	11.	77.0	448.	4.80	.83	0
28	3.	35.	20.	324.0	647.	1.60	0	0
29	3.	35.	20.	405.0	706.	.04	-0	0
30	3.	35.	11.	81.0	1233.	4.80	.83	0
31	3.	11.	11.	38.5	646.	28.80	-0	37.00
32	3.	10.	10.	38.5	583.	56.70	32.00	12.00
33	3.	10.	11.	38.5	517.	.88	-0	51.00
34	3.	12.	11.	77.0	751.	7.20	-0	-0
35	3.	20.	11.	38.5	359.	96.00	33.00	268.00
36	3.	21.	10.	77.0	728.	.04	-0	0
37	3.	23.	11.	77.0	687.	6.40	-0	0
38	3.	30.	10.	38.5	542.	4.00	80.00	0
39	3.	32.	10.	38.5	990.	3.30	60.00	0
40	3.	32.	13.	-0	506.	7.20	.78	0
41	3.	40.	10.	77.0	898.	-0	-0	0
42	3.	40.	13.	-0	1167.	8.00	60.00	0
43	4.	40.	10.	77.0	817.	3.20	75.00	0

Table 2.

	COND	PH	NA	K	NH4N	CA	MG	CL	NO3N	SO4S	TP
1	16.3	4.66	.09	.11	.39	.27	.02	.34	.38	.46	7.00
2	11.3	4.93	.15	.53	.22	.18	.05	.40	.22	.35	31.00
3	7.3	4.99	.07	.08	.09	.08	.01	.17	.14	.14	8.90
4	10.0	4.92	.11	.07	.21	.13	.03	.32	.18	.29	8.70
5	8.0	5.18	.09	.07	.14	.25	.05	.31	.18	.29	15.20
6	12.8	7.19	.42	.19	.13	.76	.48	.23	.12	.17	12.30
7	10.6	5.78	.20	.30	-0	.60	.11	.43	.24	.44	47.80
8	100.0	7.63	14.80	.76	-0	3.50	2.21	6.10	.18	9.50	26.80
9	18.3	4.49	.13	.12	.17	.28	.02	.19	.56	.34	10.10
10	12.7	4.72	.22	.14	.10	.26	.03	.32	.34	.28	16.10
11	11.3	4.95	.11	.11	.27	.27	.05	.15	.45	.31	10.40
12	11.5	6.28	.17	.16	.25	1.09	.17	.19	.50	.53	24.10
13	11.5	6.28	.17	.16	.25	1.09	.17	.19	.50	.53	24.10
14	14.9	6.80	.30	.41	.14	1.50	.35	.35	.34	.63	60.90
15	12.0	6.16	.07	.14	.10	.75	.16	.47	.21	.36	47.30
16	97.3	6.29	6.35	1.32	.41	4.58	-0	1.40	5.30	8.23	271.00
17	520.0	7.90	.95	.19	.03	5.70	1.95	.42	.77	4.22	224.00
18	12.8	4.82	.07	.20	.23	.34	.04	.20	.47	.31	22.60
19	14.6	4.64	.07	.06	.06	.13	.02	.08	.49	.22	8.00
20	11.7	6.60	.22	.11	.27	.89	.31	.15	.64	.39	15.00
21	8.9	6.25	.12	.12	.09	.90	.20	.11	.46	.19	8.00
22	8.9	6.25	.12	.12	.09	.90	.20	.11	.46	.19	8.00
23	13.3	4.61	.07	.06	.10	.10	.01	.07	.37	.22	5.90
24	13.3	4.61	.07	.06	.10	.10	.01	.07	.37	.22	5.90
25	16.9	4.53	.14	.06	.11	.16	.02	.08	.49	.22	7.30
26	14.7	4.60	.04	.04	.07	.13	.02	.18	.40	.24	6.80
27	19.0	4.48	.08	.06	.17	.43	.32	.26	.46	.48	8.60
28	22.6	4.38	.03	.04	.20	.12	.01	.11	.31	.68	2.70
29	20.9	4.40	.04	.03	.17	.19	.01	.07	.35	.60	3.60
30	25.5	4.28	.14	.07	.47	.38	.02	.37	.69	.74	11.10
31	46.6	6.49	1.04	.52	.28	2.20	2.47	.47	.62	4.58	35.20
32	11.3	6.08	.10	.10	.23	.98	.19	.19	.50	.59	52.90
33	21.4	6.86	.21	.24	.53	1.96	.46	.26	.61	1.07	104.80
34	10.0	6.59	.12	.24	.30	.78	.17	.31	.44	.48	36.70
35	37.3	7.79	.56	1.74	.23	.62	3.28	1.06	.49	.42	31.30
36	13.4	4.69	.06	.06	.44	.24	.02	.19	.39	.26	13.90
37	12.3	4.90	.16	.14	.21	.36	.15	.19	.45	.29	17.00
38	14.2	4.54	.02	.04	.14	.13	.04	.11	.34	.30	5.50
39	14.3	4.58	.07	.07	.28	.19	.01	.22	.31	.43	11.70
40	15.2	4.49	.05	.04	.23	.11	.01	.20	.36	.26	6.10
41	17.0	4.51	.05	.09	.36	.11	.01	.18	.47	.49	6.80
42	14.6	4.85	.15	.18	.27	.15	.06	.98	.27	.37	31.40
43	15.7	4.49	.04	.04	.13	.12	.02	.24	.40	.24	6.90